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Study of Polyaromatic Hydrocarbons Emitted in the Fly Ash from Coal Combustion in a Fluidized Bed Combuster

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STUDY OF POLYAROMATIC HYDROCARBONS EMITTED IN THE FLY ASH FROM COAL COMBUSTION IN A FLUIDIZED BED COMBUSTOR

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STUDY OF POLYAROMATIC HYDROCARBONS EMITTED IN THE FLY ASH FROM COAL COMBUSTION IN A FLUIDIZED BED COMBUSTOR

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STUDY OF POLYAROMATIC HYDROCARBONS EMITTED IN THE FLY ASH FROM COAL COMBUSTION IN A FLUIDIZED BED COMBUSTOR

Rebecca Heltsley August 2000 59 Pages

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Exposure to Polyaromatic Hydrocarbons (PAHs) has long been identified as an environmental concern because of their carcinogenic and mutagenic effects. The Environmental Protection Agency (EPA) has developed a list of 16 PAHs that are found on the Priority Pollutant List due to the extensive amount of data suggesting the hazards of these compounds. These toxic compounds are often emitted into the atmosphere by anthropogenic sources, such as combustors. Therefore, analysis of these compounds must be conducted during coal combustion.

Two 1000-hour coal combustion burns were performed using the 0.1 MW_{th} bench-scale fluidized bed combustor (FBC), which is found in the Combustion Laboratory at Western Kentucky University. The data contained in this thesis were collected from burning coal 97025 and coal 99626 for 1000-hour experiments. The fly ash produced from the combustor was examined as the media for the PAHs. It was collected by an in-situ cyclone sampler that was attached to various ports along the combustor during specific conditions in the combustor.

Once the fly ash was collected it was analyzed with two different extraction methods. Solvent extraction was the first method used in this study. Dichloromethane was the solvent used to extract the PAHs in the fly ash. Once the extraction was completed, GC/MS in the selective ion monitoring (SIM) mode was used to analyze the extract. The other method used to extract the PAHs from the fly ash was the thermal extraction method. This method allows direct analysis of the PAHs without any use of a solvent. The GC/TOFMS was used to analyze the samples that were extracted by the thermal extraction method.

In this study, the effects of combustion temperature, combustion bed height, sampling height, excess air ratio, and fluidizing velocity were examined to determine how each of these parameters affected the release of PAHs in the fly ash. The results indicated that the parameters investigated have a major influence on the production of PAHs in the combustor. As combustion efficiency decreases, larger PAHs (four to five fused rings) are detected in the fly ash; whereas, during high efficiency combustion, smaller PAHs (two to three fused rings) are more likely to be detected.

CHAPTER I

INTRODUCTION

A. Background

The consumption of electrical energy currently accounts for over 10% of U.S. energy end use, and over 50% of this electricity is produced from coal power plants. Producing electricity through the combustion of coal is one the oldest and cheapest methods to produce electricity. While conventional supplies of oil and natural gas are expected to run out in the near future and nuclear power has seen stagnant growth, coal supplies are plentiful and will be available to produce electricity for hundreds of years.[1]

Combustion, a complex combination of chemical reactions, heat transfer, and mass transfer, is a process that has become virtually essential to today's civilization. The evolution of the combustor has developed a means of generating heat that may be used to produce electricity or process heat, or may be used to fuel industrial processes such as cement or lightweight aggregate production or industrial boilers. It is also particularly effective for destroying hazardous organic wastes and reducing waste volume and mass, thus aiding in safe ultimate disposal.[2] Unfortunately, along with all the benefits that have evolved with the combustor, burning coal is not without its disadvantages. Combustion is one of the dirtiest methods of producing electricity, and there is a growing concern with the emissions that this process has introduced into the environment.

The burning of fuel can produce a variety of chemicals, which are harmful to the environment. Combustion pollutants include, but are not limited to, gases and particles that come from burning materials. Several of the major combustion pollutants that have been extensively examined are carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter (PM10).[3] The emission of sulfur oxides is largely dependent on the amount of sulfur the coal possesses. The release of carbon monoxide is related to the efficiency of the combustor. Nitrogen oxides are not only dependent on the amount of nitrogen present in the coal but also can be produced under specific conditions in the combustor.[4] The emission of each of these pollutants is extremely important to monitor and control. However, along with the awareness that grows with the conventional pollutants associated with the combustor, there is a growing concern with the release of volatile organic compounds, VOC, or semi-volatile organic compounds, SVOC. Polycyclic aromatic hydrocarbons (PAHs), sometimes called polynuclear aromatic hydrocarbons (PNAs), are included in this classification of compounds.[5]

PAHs are a large group of chemicals that are formed during incomplete burning of coal, oil and gas, garbage, and other organic substances like tobacco or charbroiled meat.[6] PAHs can be produced by natural or anthropogenic sources.[7] PAHs, as stated, are produced naturally by the environment. Natural sources of PAHs include events such as volcano releases and biomass burning (forest fires). Anthropogenic sources include incomplete fossil fuel combustion, industries, automobile exhaust, aviation exhaust, and cigarette smoking. Although cigarette smoke accounts for the highest exposure threat to humans, vehicle exhaust is the main source of PAHs in the environment. Table 1 provides an indication of the sources of PAHs in the United States. The primary use for

most of these chemicals is related to research purposes. However, some of the smaller PAHs are used in making dyes.[6]

Table 1. Sources of PAHs and Percentages of Total Intake[8]

Source	Percentage
Vehicle Traffic	35
Aluminum Production	17
Forest Fires	17
Domestic furnaces	12
Coal Production	11
Energy Production	6
Waste Incineration	3

PAHs are a group of more than a hundred organic compounds composed of two or more fused carbon rings derived from benzene. As a rule, when PAH compounds grow in molecular weight, their solubility in water decreases, solubility in fat tissue increases, and their melting and boiling points increase. They have been identified in soil, surface water, groundwater, sediment, and air. Generally, PAHs are very hydrophobic organic compounds and are relatively insoluble in water. They have a high affinity for organic matter and, when present in soil or sediments, tend to remain bound to particles and dissolve slowly in water. Soil, sediment, and suspended particulate matter represent important media for the transport of these chemicals.[9]

Exposure to PAHs has long been identified as an environmental concern. Over 120 PAHs have been detected in urban pollution. Of these 120, there are 16 PAH compounds (Figure 1) that the U.S. Environmental Protection Agency (EPA) has classified as priority pollutants.[10] Table 2 lists the parameters that are associated with the sixteen PAHs classified as priority pollutants. PAHs are not commonly associated with adverse health affects in humans. However, the U.S. Department of Health and Human Services has determined that some PAHs, particularly 4- and 6-ringed PAHs, can potentially cause cancer.[7]

PAHs are present in low concentrations virtually everywhere in the environment.[8] Therefore, exposure to PAHs can not be eliminated. However, due to their toxicity and carinogenicity, restrictions over the release of PAHs, by the EPA, are continually being examined. Therefore, detailed studies such as the present one have been conducted researching the release of PAHs from combustion systems.

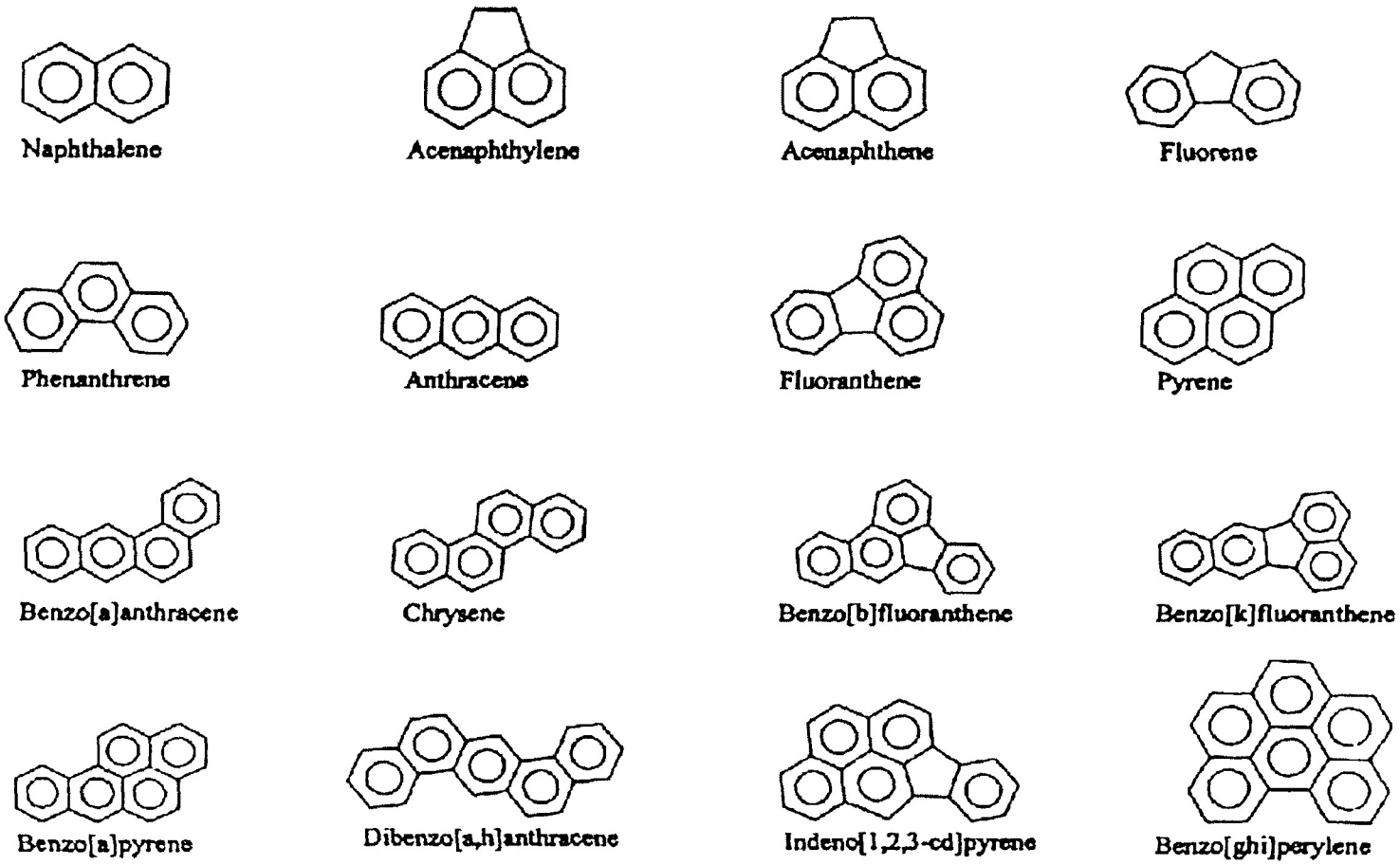

Figure 1. The structure of 16 EPA specified Priority PAH pollutants

Table 2. Basic Parameters of the 16 Target PAHs*

Compond	Formula	MW	B.P. (°C)	H_f(Kcal/mol)
Naphthalene	$C_{10}H_8$	128	218	40.58
Acenaphthylene	$C_{12}H_8$	152	280	80.74
Acenaphthene	$C_{12}H_{10}$	154	279	42.59
Fluorene	$C_{13}H_{10}$	166	298	54.36
Phenanthrene	$C_{14}H_{10}$	178	340	57.44
Anthracene	$C_{14}H_{10}$	178	340	62.92
Fluoranthene	$C_{16}H_{10}$	202	384	87.92
Pyrene	$C_{16}H_{10}$	202	n.a.	67.34
Benz[a]anthracene	$C_{18}H_{12}$	228	438	99.46
Chrysene	$C_{18}H_{12}$	228	448	88.85
Benz[b]fluoranthene	$C_{20}H_{12}$	252	n.a.	103.24
Benz[k]fluoranthene	$C_{20}H_{12}$	252	n.a.	105.07
Benz[a]pyrene	$C_{20}H_{12}$	252	495	87.51
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	n.a.	116.34
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278	524	101.49
Benz[ghi]perylene	$C_{22}H_{12}$	276	n.a.	91.31

* MW – molecular weight;

B.P. – boiling point;

Hf – the heat of formation;

n.a. – not available

Fluidized bed combustion (FBC) is one of several advanced approaches for substantially improving the efficiency of coal-fired power systems, while significantly reducing emissions. This reduction in emissions is highly favored due to the increased restrictions that are being imposed on the concentration of gaseous pollutants, such as NO_x and SO_2. The advanced technology employed by FBC systems allows power plants to burn lower rank coals while at the same time addressing environmental and economic concerns.

FBC systems allow for an increased coal and air interaction in the combustion chamber in order to maximize the combustion efficiency. In FBC, crushed coal is injected into a bed above a grate-like air distributor. Air is injected upward through the grate lifting and suspending the solid particles. The bed continues to expand allowing a greater airflow rate until an equilibrium position is reached. At this point, the particles can move freely, and the bed behaves like a fluid. Air moves upward through the relatively dense fluid-like particles serving to rapidly mix any materials being added to the bed and transfer heat rapidly from one position of the bed to another.

As indicated before, FBC systems have a number of advantages over other combustion techniques. Limestone is added directly to the fluidized bed—thereby allowing it to actively absorb sulfur dioxide, a major pollutant from sulfur deposits in the coal. Limestone reacts with the sulfur dioxide and oxygen to produce calcium sulfate, which accounts for approximately 90% reduction in sulfur dioxide emissions.

In an FBC system, the height of the bed materials, which are suspended above the bottom of the combustor, is a function of the fluidizing velocity of the air entering the combustor below the bed. FBC systems generally have a continuous feeding system of

limestone and coal and require that bed ash be removed at a specific rate to sustain the proper amount of bed material for economic operation. The temperature is controlled in an FBC system. It usually ranges anywhere from 700°C to 950°C. By controlling the temperature, FBC systems emit a smaller concentration of NO_x in the flue gases when compared to other combustors, such as the Pulverized Coal boiler (PC).[11]

Although technology allows for many evident environmental and economic advances in the FBC system, it can not be ignored that combustor systems, in general, are one of the major anthropogenic sources of PAH emissions. With the EPA regarding 16 PAHs as priority pollutants and their known carcinogen effect, it is imperative that research is conducted concerning the emission of PAHs from combustor systems to evaluate how the release of these pollutants can be minimized. Therefore, this study was performed to further examine the release of PAHs in the fly ash of the combustor.

Fly ash is a coal combustion byproduct. It consists of small particles, which are primarily made up of silicon, aluminum, iron, and calcium oxides. The particles are generally less than 250 micrometers in size and are spherical in shape. They have a high mechanical strength and a melting point greater than 1000°C. Coal fly ash can be utilized in concrete and can replace clay, sand, limestone and gravel, and save the energy costs of mining such materials. However, fly ash can serve as a source of pollution as well. When PAHs are formed in the combustor due to incomplete combustion of carbon compounds, they may attach to small particles, such as fly ash, and be transported considerable distances.[8]

B. Formation of PAHs in Coal Combustion

PAH compounds are major contributors to air pollution from combustion sources. Basic understanding of the factors that govern the detailed chemical composition of the effluents from combustion systems is necessary for the identification of signatures for source attribution and the development of control strategies. Several mechanisms have been examined to better understand how PAHs are being generated in combustion.

Complete combustion of fossil fuels should result in the production of carbon dioxide and water at oxidation conditions. However, the combustion process is highly complex and complete degradation of the coal rarely occurs. Therefore, large organic compounds including PAHs may be released from the combustor.

Incomplete combustion of fossil fuels has been deemed as a major source of PAH formation. PAHs can be formed either during pyrolytic processes or combustion processes, where pyrolysis is the process proceeding combustion.[11] As the coal matrix is heated, chemical and physical changes occur to the structure of the coal. These transformations that occur to the coal result in the release of organics. The organics released then undergo cyclization reactions, which lead to the production of polycyclic aromatic hydrocarbons that can exist in the gas and/or the solid phase of the effluents released from the combustor.[12]

There are three mechanisms that have been examined thoroughly by which PAHs may be formed during coal combustion.[13-15] Each of the mechanisms is highly regarded as being a source of producing PAHs. However, determining which mechanism occurs readily depends upon the combustion conditions and the fuel type. The first mechanism is known as the breakdown reaction. In this mechanism the coal matrix breaks down

during inefficient combustion and releases single multiple benzene ring compounds (PAHs) that were initially part of the complex coal matrix.[13] The second mechanism involves a series of reactions that may occur under pryrolytic conditions. It is often referred to as the condensation reaction. In this reaction, there are small ring systems condensing anywhere in the combustion zone to favor the production of PAHs.[14] The third mechanism involves the cyclization of carbon chains and subsequent ring addition that may result in the production of PAHs, hence, the name, cyclization reaction.[15]

As can be seen, there are a variety of pathways in which PAHs may form during coal combustion. However, not only must the pathways be examined the emission of PAHs will also be affected by the combustion variables (temperature, airflow rate, percent oxygen) and the characteristics of the reactor.[16] Taking all of these factors into consideration, it can easily be observed that the sampling and measuring of the emission of PAHs may be linked to many complications.[17] These problems and the low concentrations in which PAHs are present in the fly ash make it necessary to use very sensitive analysis methods.

C. PAH Analysis in the Solid Phase

1. Extraction of the PAHs

Extraction of PAHs can be executed by several techniques. A very common method used to perform an extraction of PAHs is a solvent extraction. Solvent extraction with organic liquids is routinely employed to obtain the PAHs in a solution in order to perform the required analysis of the samples. The concentration of PAHs in the fly ash is usually extremely low (ppb range) and a very sensitive and selective analysis method

be employed to obtain the most accurate results. When using the solvent extraction method, preconcentration of the sample is required in order to achieve the necessary sensitivity level before analyzing with a conventional instrumental method.[18]

Another method of extraction, which is becoming highly attractive for the analysis of solid samples, is thermal extraction. Thermal extraction is a solventless method that is designed to heat small quantities of solid samples. The operator can determine the heating rate of the sample. Once the sample has been heated, the volatile components of the sample are quickly transported out of the heating apparatus and swept into the transfer line, which will lead to the analysis method that is preferred.[19]

2. Analysis Methods

There are a variety of methods that can be used when studying PAHs. However, environmental contaminants, such as PAHs, often occur in complex mixtures of very similar compounds in low concentrations, imposing stringent requirements on the method chosen for analysis. The most widely used method is the coupling of gas chromatography with either mass spectroscopy (GC/MS), time-of-flight mass spectroscopy (GC/TOFMS), or flame ionization (GC-FID).[20-27] Optimal analyses of PAHs have been accomplished using these methods.[28,29] GC/MS is very advantageous due to its increased selectivity and high sensitivity. This method also allows for the quantification and identification of PAHs at the same time. However, GC limitations are well known; a tedious sample preparation, usually compromising a Soxhlet extraction followed by purification and a concentration step, is necessary unless using the thermal extraction method. Yet, it must be considered that when utilizing the thermal extraction method coupled with the GC/MS, very little sample preparation is needed.

Another method being used to analyze PAHs is the two-step laser mass spectroscopy (L2MS). It offers several advantages over conventional methods.[30] This method requires little to no sample preparation, and direct chemical analysis of complex environmental samples is possible. This system allows for the measurement of samples, such as PAHs, within minutes in a low ppb range.[31] Thus, it is evident that the L2MS system opens new perspectives for a better understanding of complex mixtures such as PAHs.

D. Purpose of This Study

In this study, PAH emissions in the fly ash from an FBC system at the Combustion Laboratory at Western Kentucky University were evaluated and compared from two separate runs with solvent extraction and thermal extraction coupled with GC/MS and GC/TOFMS analyses, respectively. The objective of this experiment was to examine how the content of PAHs in the fly ash varied with different combustion parameters. These parameters included temperature, combustion bed height, fluidizing velocity, excess air ratio, and coal feeding rate. The total content of PAHs was examined as well as the distribution of PAHs in the samples.

CHAPTER II

EXPERIMENTAL

A. Collection of the Fly Ash Samples

Fly ash samples were collected using a high efficiency cyclone to trap the fly ash. The cyclone was attached to one of the sampling ports along the freeboard zone of the combustor (the same port was used for each individual testing condition). By using a vacuum, it allows the flue gas to be drawn from the freeboard space of the combustor through the sampling port and into the cyclone. The flow rate was approximately 1.79 L/sec. Once the flue gas enters the cyclone, the fly ash was separated from the gas due to the centrifugal force and the fly ash was then collected in the bottom of the container. The average sampling time was approximately thirty minutes. Sampling for the fly ash began eight hours after changing the testing conditions and stabilizing the combustor.

B. Materials

1. Reagents

The following reagents were utilized in this experiment: standard PAHs mix, 2000 μg/mL each in methylene chloride:benzene (50:50) (Cat. No. 48905-U), naphthalene-d8, 2000 μg/mL in methylene chloride (Cat. No. 48715-U), anthraene-d10, 2000 μg/mL in methylene chloride (Cat. No. 48863) and benzo[a]anthracene-d-12, 2000

μg/mL in methylene chloride (Cat. No. 48789). Each of the reagents listed above was purchased from SUPELCO Inc. (Pa, USA). Methanol (purge and trap grade, Cat. No. 48093) and methylene chloride (capillary GC grade, Cat. No. 41475-1) were purchased from Aldrich Chemical Com., Inc. (WI, USA).

2. Coals and Limestone

During this experiment, two coals (WKU number 97025 and WKU number 99626) were evaluated and compared. Each coal was tested for 1000 hours. The characteristics of the two types of coals and the Kentucky limestone that were used in each of the 1000-hour runs are listed in Table 3.

3. Apparatus

There were two types of extraction apparatus used in this experiment. One apparatus utilized the Tecator Soxhlet 1045 extraction system; the other method of extraction was the thermal extraction system. The Soxhlet extraction system required the use of sample vials, which were 2 mL (Cat. No. 27344) with polytetrafluoroethylene (PTFE)-lined caps and precleaned amber glass. The vials were purchased from SUPLECO Inc. An extraction thimble and –60 mesh sieves were used for this apparatus.

The ThermEx Inlet system apparatus has several accessories that were needed to operate this system. A muffle furnace tray holder was required to hold the porous fused quartz sample crucibles while cleaning in the furnace. The furnace was a model FB 1300 (Barnstead Thermolyne Corp., IA, USA). The crucibles were handled with stainless steel forceps and stored in quartz petri dishes inside a dessiccator. An analytical balance was needed to weigh out the sample and a mortar and pestle was used to grind the fly ash sample. Once ground, a sieve -60 mesh in size was used to filter the fly ash for the

solvent extraction method, and a sieve of –100 mesh was used to filter the fly ash for the thermal extraction method.

C. Combustion Runs

The experiments were conducted with Western Kentucky University's 0.1 MW_{th} bench scale fluidized bed combustor (Figure 2). It has a 0.3-meter ID and a 4.0-meter effective height. The combustion bed zone is the area of the combustor where the fuel was added and fluidized, it is also known as the dense zone. The freeboard zone in the combustor is 2.5 meters high. Having the freeboard zone this length allows sufficient residence time for the combustion of fine particles, which may be contained in the flue gas from the dense zone. Coal was fed into the system by means of an under-bed auger, which is under positive pressure. Primary air was injected into the combustor from the bottom of the combustor; whereas, secondary air was injected into the combustor in the freeboard zone, which is one meter above the bed. The secondary air was injected in a direction which is tangent to the inner surface of the combustor. Six active heat exchange tubes were used to control the temperature of the bed. There are several principle components of the fluidized bed combustor such as the combustor itself, the fuel bunkers, heat exchangers, wet scrubber, air supplying system, and the stack. For a more detailed explanation of WKU's FBC system, refer to Weilan Pan's master's thesis.[32] A total of seven 1000-hour runs have been performed with this FBC system. The experimental data used in this study was from the third (Coal number 97025) and the seventh (Coal number 99626) combustor runs.

Table 3. Proximate and Ultimate Analyses Values for the Coals and Limestone Used in the Study.

	Coal 97025	Coal 99626	KY Limestone
Proximate Analysis (%)			
Moisture	4.56	6.96	0.06
Ash	10.97	13.81	56.9
Volatile Matter	36.25	34.14	n/a
Fixed Carbon	52.78	52.05	n/a
Ultimate Analysis (%)			
Ash	10.79	13.81	56.9
Carbon	74.69	69.53	9.06
Hydrogen	4.95	4.49	0.00
Nitrogen	1.63	1.55	0.00
Sulfur	3.06	4.48	0.00
Oxygen	4.50	5.73	34.04
Miscellaneous Analysis			
Chlorine (ppm)	0.21	0.41	n/a
Calorific Value (BTU/lb)	13152	12406	n/a

*Moisture is as-received, all other values are reported on a dry basis. Unless otherwise noted, all values are given in percent by weight

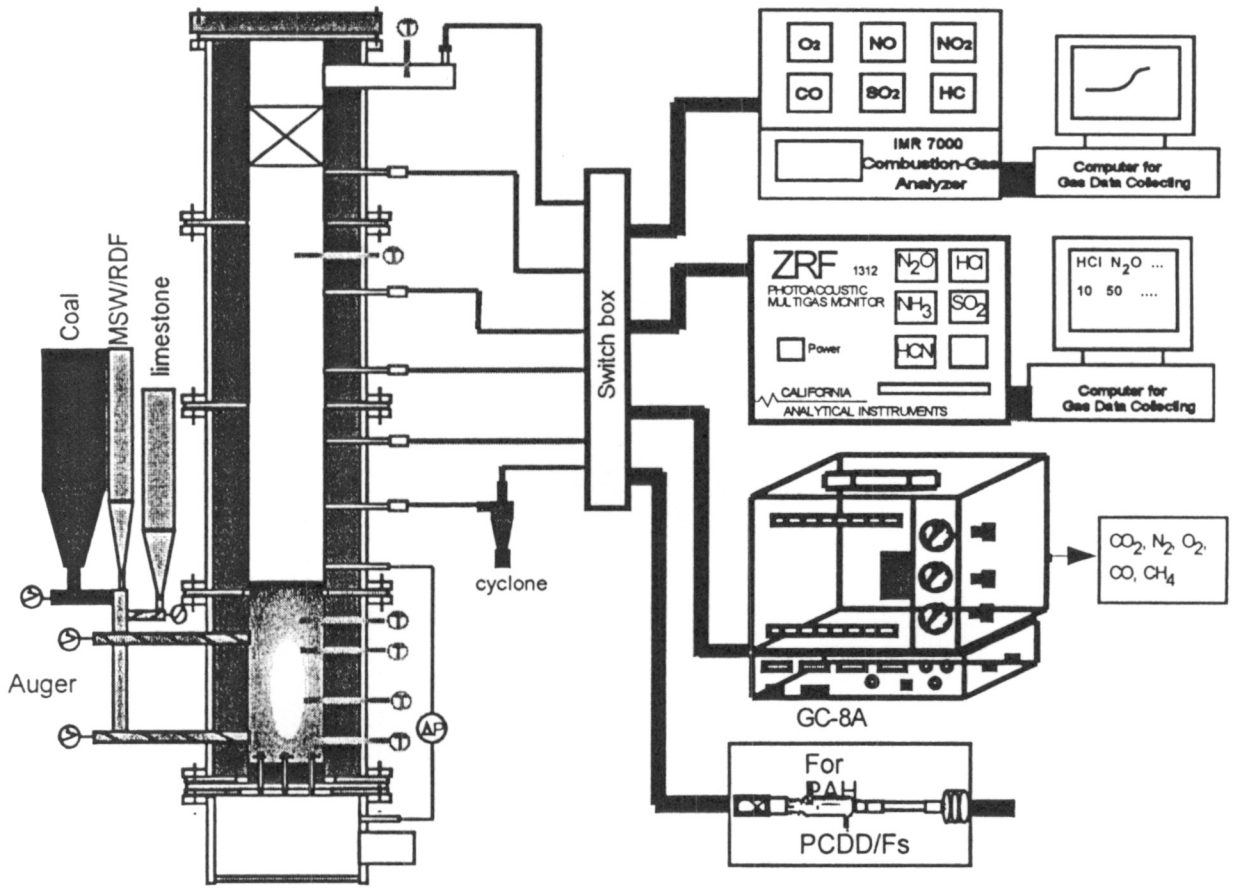

Figure 2. Schematic Diagram of Western Kentucky University's fluidized bed combustor.

D. Analysis

1. Solvent Extraction Followed by GC/MS

The fly ash samples that were collected under specific operating conditions during the first run were extracted using a Tecator Soxtec 1045 extraction system. Then for each condition, 6 to15 grams of the –60 mesh (250 μm) ash were positioned in the extraction thimble with dichloromethane. The extractor was then heated to 120°C in order to extract materials from the ash for a period of one hour. Once heated, the thimble and the ash were removed from the apparatus and the extract was heated with the refluxing dichloromethane (80 mL) for five more hours. After five hours, the extracted solution was then condensed and moved to a 10 mL volumetric flask.

Once the extraction was completed, a Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for GC/MS analysis. 2 μL aliquots of the samples were injected in the splitless mode onto the RTX-5 fused silica capillary column (60 m x 0.32 mm and a stationary phase thickness of 1.0 μm). The carrier gas was helium. The surrounding temperature for the interface, injector, and detector was 230°C. The mass spectrometer was operated in two modes, the scan mode and the selected ion monitoring (SIM) mode. The scan mode was used for determining the PAHs retention times and the SIM mode was used for the analysis of the PAHs. The quantitative analysis was performed using calibration curves of the PAH standards. The temperature programming and the pressure program parameters for the GC are listed in Tables 4 and 5. The quantitative analysis was carried out using the calibration data (Table 6) of the PAHs standards, which contained the sixteen PAHs specified by the EPA.

Table 4. GC Temperature Program for PAH Analysis.

Rate (°C/min)	Temp. (°C)	Time (min)
	70	1.00
8.00	150	0.00
5.00	250	5.00
7.00	300	5.00

Table 5. GC Pressure Program for PAH Analysis.

Rate (kPa/min)	Press. (kPa)	Time (min)
	106.50	1.00
2.90	135.90	0.20
1.20	147.50	5.00
1.00	157.30	5.00

Table 6. The Calibration Data for the Sixteen PAHs specified by EPA.

	Peak Area			
Compound Name	10 (ng/μg)	50 (ng/μg)	100 (ng/μg)	200 (ng/μg)
Naphthalene	5028	21994	46227	83208
Acenaphthene	4709	28416	58742	125751
Acenaphthene	5871	23008	52109	120967
Fluorene	8304	42012	83640	196402
Phenanthrene	9820	43362	84098	182693
Anthracene	5912	26380	56272	121354
Fluoranthene	4603	24963	47394	89951
Pyrene	4759	22657	44297	90453
Benzo[b]fluoranthene	2017	11531	24143	52649
Chrysene	3203	13752	22905	47268
Benzo[b]fluoanthene	1518	7085	15182	33670
Benzo[b]fluoranthene	4319	19226	35479	74993
Benzo[k]pyrene	4012	15327	33046	67226
Indeno[1,2,3-cd]pyrene	1739	9631	21807	36859
Dibenz[a,h]anthracene	1823	10476	19865	39072
Benzo[g,h,I]perylene	1518	8749	16751	31199

2. Thermal Extraction Followed by GC/TOFMS

The fly ash samples that were collected under each of the specific conditions during the fifth run were extracted and analyzed using the ThermEx Inlet system and the LECO Pegasus II GC/TOFMS. A sample of about 100 mg was loaded into a quartz crucible. The quartz crucible was then placed into the ThermEx pyrocell and heated. The evolved gases formed from heating were then swept by helium to the Cryogenic Focusing System (CFS) cryocell. In the cryocell, the gases were trapped by liquid nitrogen and desorbed onto the GC capillary column and then analyzed by the GC/TOFMS.

Once the evolved gas process was completed, the gases were then transferred to the LECO Pegasus II GC/TOFMS. The GC/TOFMS is equipped with a 60,000 compound NIST data base, which was used for the analysis of the samples. Helium was the carrier gas. The capillary column used was a HP-5 (30 m x 0.32 mm x 0.25 μm). The surrounding temperature for the transfer line was 300°C. The mass spectrometer was operated with the ions selected for each of the sixteen PAHs specified by the EPA. The quantitative analysis was carried out using calibration curves of the PAH standards. The temperature programming parameters for the ThermEx Inlet system, Cryogenic Focusing System, and the GC are listed in Tables 7, 8, and 9. The quantitative analysis was carried out using calibration curves of the PAHs standards, which contained the sixteen PAHs specified by the EPA. Figure 3 illustrates an example of the calibration curves used in this study for the 3-ring PAHs. For further calibration curves of each of the PAH standards refer to Daozhong Zou's master thesis.[33]

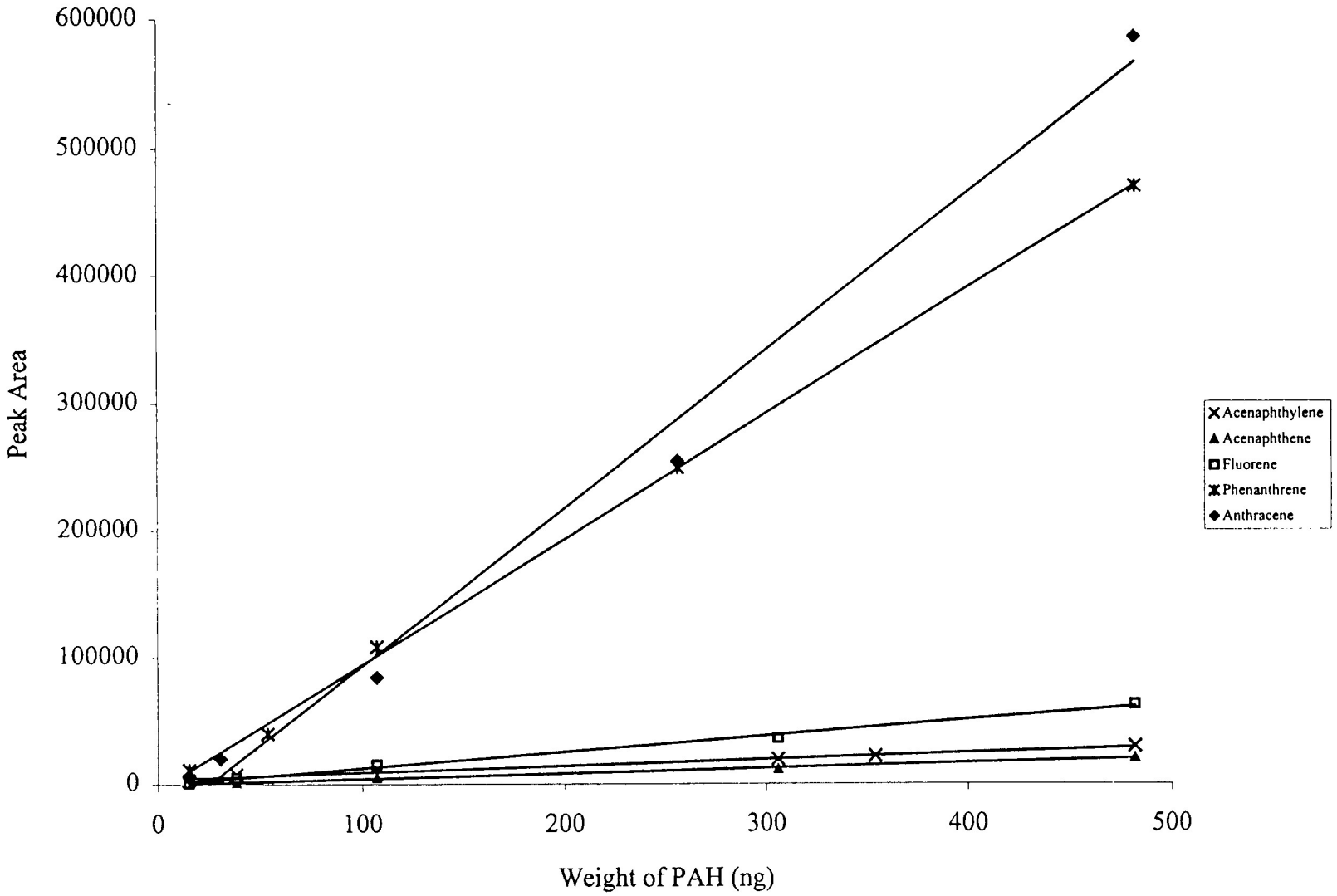

Figure 3. Calibration curves of 3-ring PAHs.

Table 7. The Temperature Programming for the ThermEx Inlet system for PAH analysis.

Start (°C)	Rate (°C/min)	End (°C)	Time (min)
60	Hold	60	0.5
60	35	280	6.3
280	Hold	280	30.0
280	35	340	1.7
340	Hold	340	3.0
340	100	60	2.8

Table 8. The Temperature Programming for the Cryogenic Focusing System for PAH Analysis.

Start (°C)	Rate (°C/min)	End (°C)	Time (min)
-50.0	Hold	-50.0	44.3
-50.0	Step	315	1.5
315	Hold	315	6.5
315	Step	-50.0	1.5

Table 9. GC Temperature Program for PAH Analysis.

Rate (°C/min)	Temp. (°C)	Time (min)
	35	44.3
35.0	315	2.0

E. Comparison of Analysis Methods.

There were two different techniques used in this study to analyze the fly ash samples. Therefore, a study in itself had to be conducted to determine how the data from each of these methods could be compared. In the solvent method, at least 6 grams of fly ash was used when analyzing the sample; however, in the thermal extraction method as little as 60 mg was used (depending on the availability of the fly ash). Upon analysis of these methods, it was found that the methods are comparable. However, sample size could affect the homogeneity of the sample and even possibly cause a difference in the individual concentration of PAHs, yet, the total concentration of the PAHs in the fly ash was found to be comparable. A complete examination of this study can be referred to in Daozhong Zou's master thesis.[33] However, the comparison of the methods was of utmost importance; the present study was done to examine how the combustion conditions effected the content of PAHs in the fly ash. The samples, which were collected and analyzed, fully represent the trends observed when specific parameters were altered during combustion runs.

CHAPTER III

RESULTS AND DISCUSSION

A. Analysis of the Samples

1. GC/MS Analysis of PAHs

A chromatogram of the sixteen PAHs that the EPA classifies as priority pollutants was obtained using the GC/MS and is shown in Figure 4. The 16 PAHs were identified using the GC/MS splitless mode. The GC peaks were identified through their respective mass spectrum using the NIST/EPA/NIH 62,000 compound database. By examining this chromatogram, the retention time and the mass spectrum of each of the 16 PAHs was obtained. In Table 10, the parameters used for the 16 PAHs are listed. The data obtained from the GC/MS analysis was from the third 1000-hour testing performed in the combustor. Throughout this paper, this data will be referred to as coal 97025.

2. GC/TOFMS Analysis of PAHs

The chromatogram found in Figure 5 was obtained with the GC/TOFMS. The chromatogram shows good separation, and the 16 PAHs were identified using the NIST Library search. The retention times and the mass spectrum of each of the 16 PAHs was obtained from this figure. Table 11 shows the parameters for the 16 PAHs. The data obtained from the GC/TOFMS was from the seventh 1000-hour testing done in the combustor. This data will be referred to as coal 99626.

Table 10. Parameters for the 16 PAHs for GC/MS Analysis.

No.	R.T. (min)	Compound Name	Selected Ion	B.p. (°C)	H_f (Kcal/mol)
1	12.480	Naphthalene	128	218	40.58
2	17.467	Acenaphthylene	152	280	80.74
3	18.092	Acenaphthene	154	279	42.59
4	19.982	Fluorene	166	298	54.36
5	24.445	Phenanthrene	178	340	57.44
6	24.683	Anthracene	178	340	62.92
7	31.138	Fluoranthene	202	384	87.92
8	32.427	Pyrene	202	na	67.34
9	40.170	Benzo[a]anthracene	228	438	99.46
10	40.542	Chrysene	228	448	88.85
11	51.483	Benzo[b]fluoranthene	252	na	103.24
12	51.761	Benzo[k]fluoranthene	252	na	105.07
13	52.692	Benzo[a]pyrene	252	495	87.51
14	54.277	Indeno[1,2,3-cd]pyrene	276	na	116.34
15	54.846	Dibenz[a,h]anthracene	278	524	101.49
16	56.089	Benzo[g,h,I]perylene	276	na	91.31

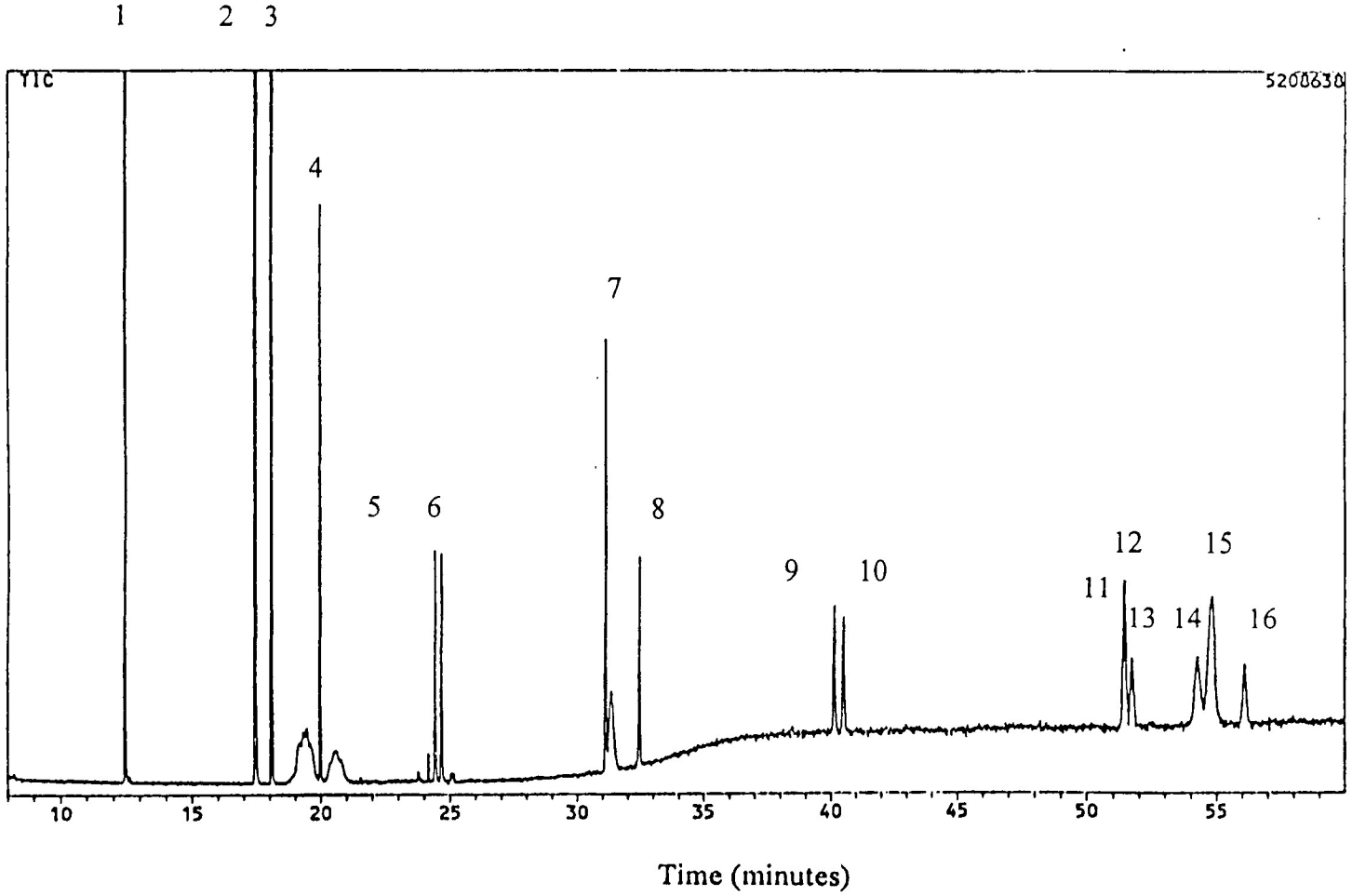

Figure 4. Standard fly ash chromatogram for GC/MS.

Table 11. Parameters for 16 PAHs for GC/TOFMS Analysis

Peak Number	Compound	Quantitation Ion	RT/second	RRT/second
1	Naphthalene-d8	136	2860.4	-
2	Naphthalene	128	2861.2	0.8
3	Acenaphthylene	152	2924.9	64.5
4	Acenaphthene	153	2932.4	72.0
5	Fluorene	166	2953.3	92.9
6	Anthracene-d10	188	2992.4	-
7	Phenanthrene	178	2993.4	0.1
8	Anthracene	178	2995.4	3.0
9	Fluoranthene	202	3044.0	51.6
10	Pyrene	202	3053.3	60.9
11	Benz[a]anthracene-d12	240	3103.0	-
12	Benz[a]anthracene	228	3104.1	1.1
13	Chrysene	228	3105.9	2.9
14	Benz[b]fluoranthene	252	3147.8	44.8
15	Benz[k]fluoranthene	252	3148.8	45.8
16	Benz[a]pyrene	252	3160.7	57.7
17	Indeno[1,2,3-cd]pyrene	276	3214.6	111.6
18	Dibenz[a,h]anthracene	278	3215.7	112.7
19	Benz[ghi]perylene	276	3229.3	126.3

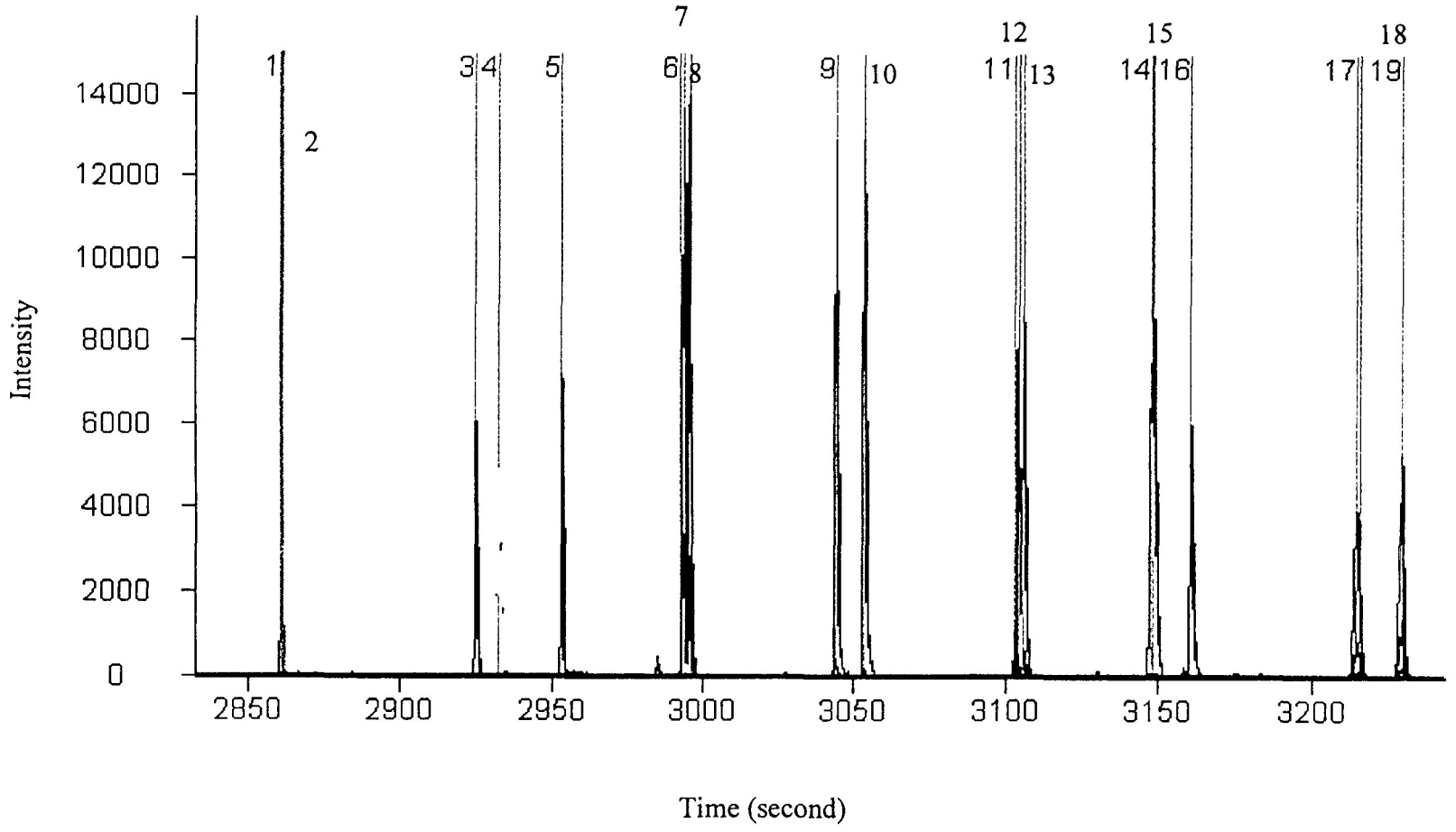

Figure 5. Standard fly ash chromatogram for GC/TOF-MS

B. PAH Emissions in the Fly Ash During Coal Combustion

1. The Effect of Combustion Temperature on the Content of PAHs in the Fly Ash for Coal 97025 and Coal 99626.

The combustion temperature has been found to be an extremely important factor affecting the efficiency of fossil fuel combustion. An increase in the combustion temperature generally results in a more efficient burn. Table 12 displays the combustion parameters for examining the effect that varying the temperature has on the release of PAHs in the fly ash for these two runs. Figure 6 demonstrates how the temperature influences the PAH emissions. In this graph, as the temperature increased, the amount of PAHs in the fly ash was steadily decreasing. As stated before, in combustion systems an increase in the temperature will improve the combustion efficiency. Therefore, this trend may have been a result of the efficiency increase, which resulted in a decrease in the PAHs emitted.[34] Also, at increased temperatures, larger organic molecules tend to almost completely decompose which would also result in the decrease of PAHs in the fly ash.[35]

Table 12. Combustion Parameters for Examining the Effect of Temperature on the PAH Content in the Fly Ash.

	Coal 97025	Coal 99626
Air Flow Rate (m/s)	4.0	4.0
Bed Height (m)	0.832	0.865
Coal Feeding Rate (rpm)	77	77
Secondary Air (m/s)	0.0	0.0
Limestone addition Rate (rpm)	11	14

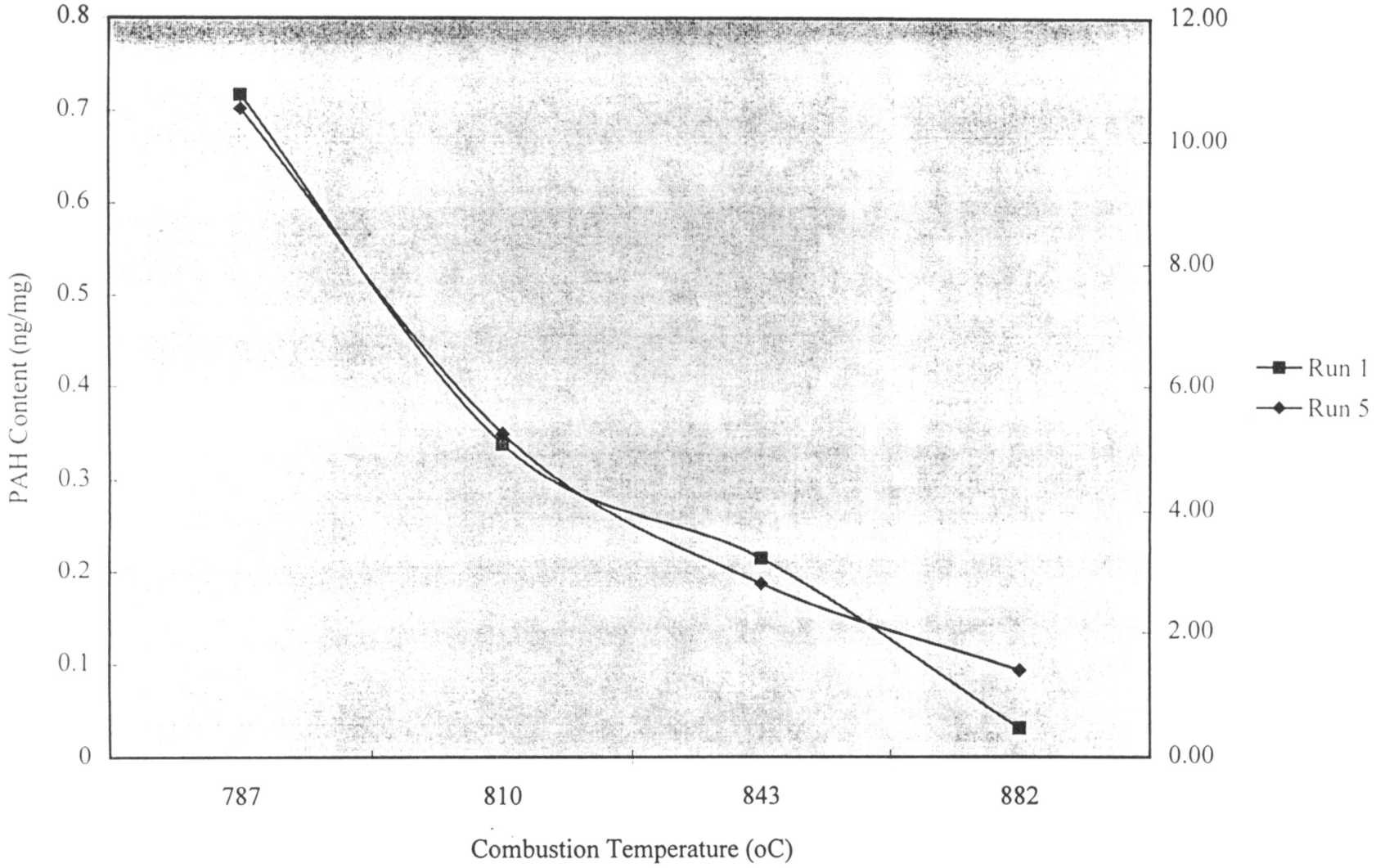

Figure 6. The effect of combustion temperature on PAH content in the fly ash in an FBC system.

2. The Effect of Bed Height on the Content of PAHs in the Fly Ash for Coal 97025 and Coal 99626.

Table 13 displays the combustion parameters used when examining the effect of bed height on the content of PAHs in the fly ash for the two 1000-hour testing runs. As the bed height increased, the PAH content in the fly ash decreased in both of the runs, as shown in Figure 7. Bed height is another factor that contributes to the combustion efficiency. As the bed height increases in the combustor, the coal particles and organics found in the combustion zone have a longer residence time. This increase in the residence time, in turn, increased the combustion efficiency. Thus, this increase in efficiency lead to the decrease observed in the amount of PAHs found in the fly ash.

3. The Effect of Sampling Height on the Content of PAHs in the Fly Ash for Coal 97025 and Coal 99626.

The combustion parameters for testing the effect the sampling height has on the content of PAHs in the fly ash for the two runs are listed in Table 14. Figure 8 illustrates the effect the sampling height has on the content of PAHs in the fly ash. By comparing the data from the selected sampling ports along the combustor, it was evident that the total amount of PAHs reduced sharply with an increase in the height from the distributor. These results suggested that as PAHs in the combustor have a longer residence time in the furnace and the combustor was operating under oxygen rich conditions, the PAHs may be decomposing to other products such as CO_2 and H_2O as they are transported along the freeboard zone.

Table 13. Combustion Parameters for Examining the Effect of Bed Height on the PAH Content in the Fly Ash.

	Coal 97025	Coal 99626
Air Flow Rate (m/s)	4.4	4.4
Temperature (°C)	810	799
Coal Feeding Rate (rpm)	78	77
Secondary Air (m/s)	0.0	0.0
Limestone addition Rate (rpm)	11	14

Table 14. Combustion Parameters for Examining the Effect of Sampling Height on the PAH Content in the Fly Ash.

	Coal 97025	Coal 99626
Air Flow Rate (m/s)	4.4	4.4
Temperature (°C)	810	799
Coal Feeding Rate (rpm)	78	77
Secondary Air (m/s)	0.0	0.0
Bed Height (m)	0.82	0.86
Limestone addition Rate (rpm)	11	14

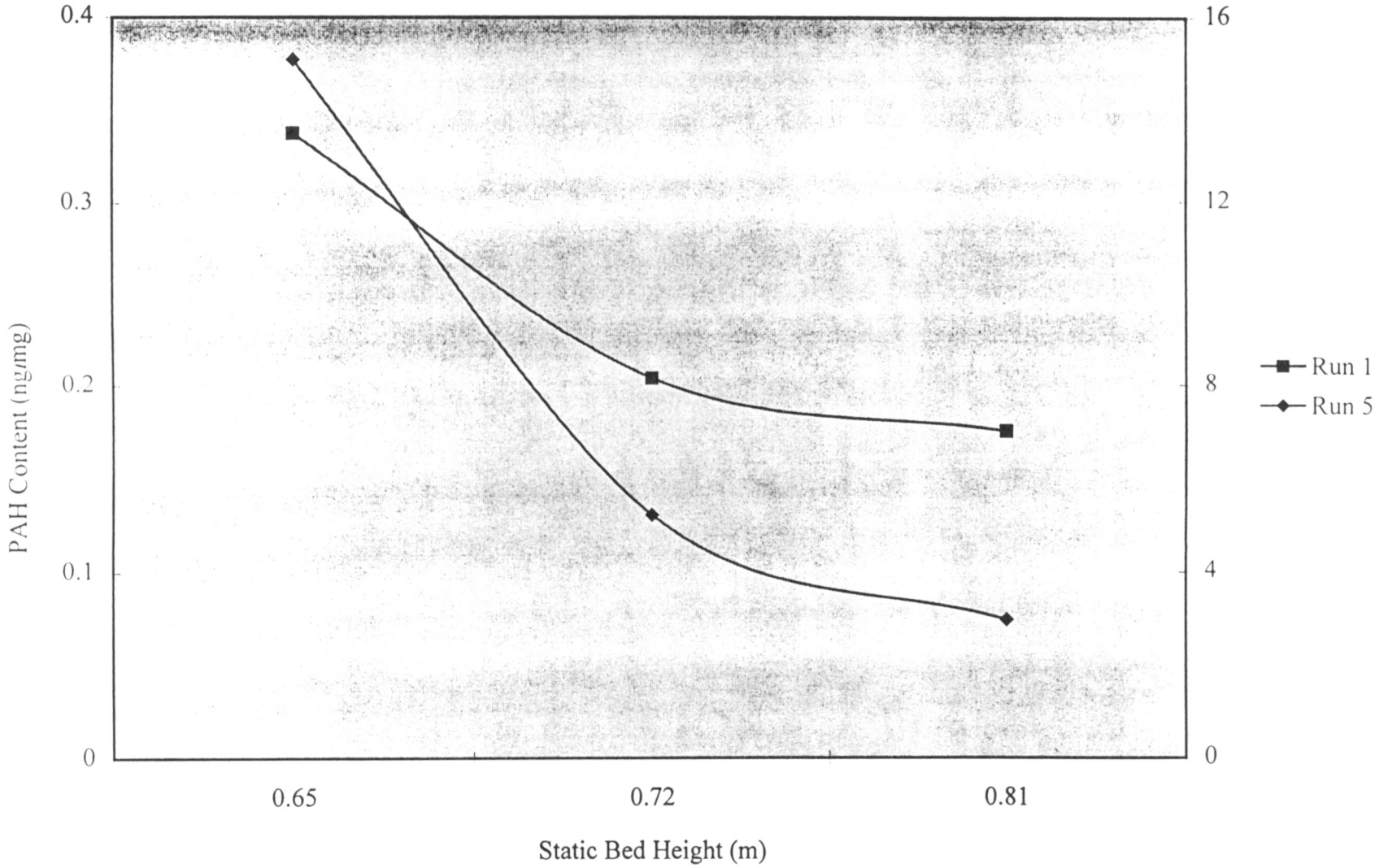

Figure 7. The effect of bed height on PAH content in the fly ash in an FBC system.

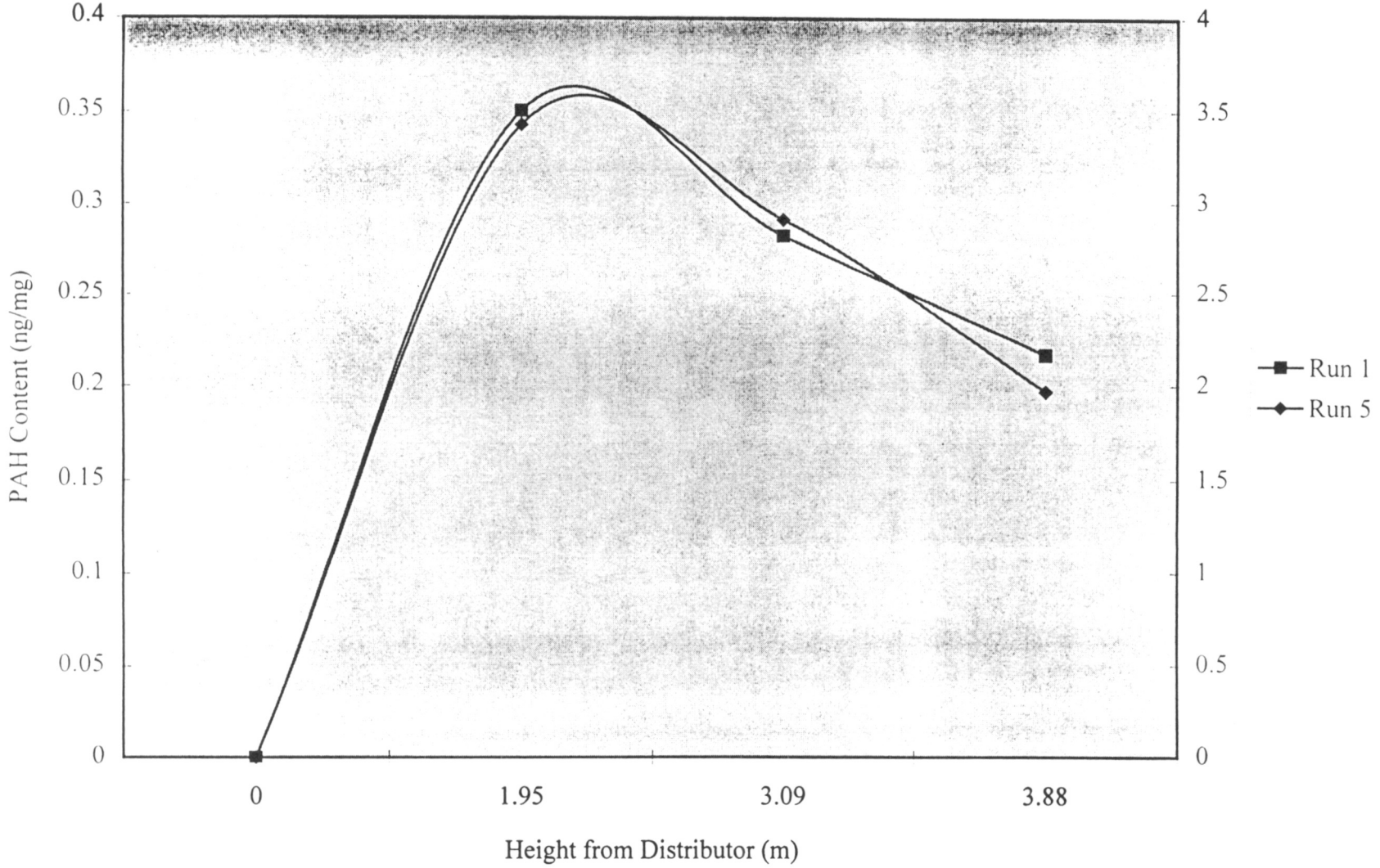

Figure 8. The effect of sampling height on PAH content in the fly ash in an FBC system.

4. The Effect of Excess Air Ratio on the Content of PAHs in the Fly Ash for Coal 97025.

The combustion parameters for testing the effect the excess air ratio has on the content of PAHs in the fly ash for the first run are shown in Table 15. Figure 9 displays the content of PAHs in the fly ash versus the excess air ratios. As can be observed from the figure, there was a dramatic increase in PAHs at the lower excess air ratios. Low excess air ratios indicate a low amount of oxygen found in the surrounding atmosphere of the combustor. The inadequate amount of oxygen adversely affects the combustion efficiency. However, as the excess air ratio increased, the oxygen became more readily available in the combustor and therefore made the efficiency increase. The efficiency increase resulted in a sharp decrease in the release of PAHs found in the fly ash sample.

Table 15. Combustion Parameters for Examining the Effect of Excess Air Ratio on the PAH Content in the Fly Ash for Coal 97025.

	Coal 97025
Air Flow Rate (m/s)	4.0
Temperature (°C)	810
Secondary Air (m/s)	0.0
Bed Height (m)	0.82
Limestone Addition Rate (rpm)	11

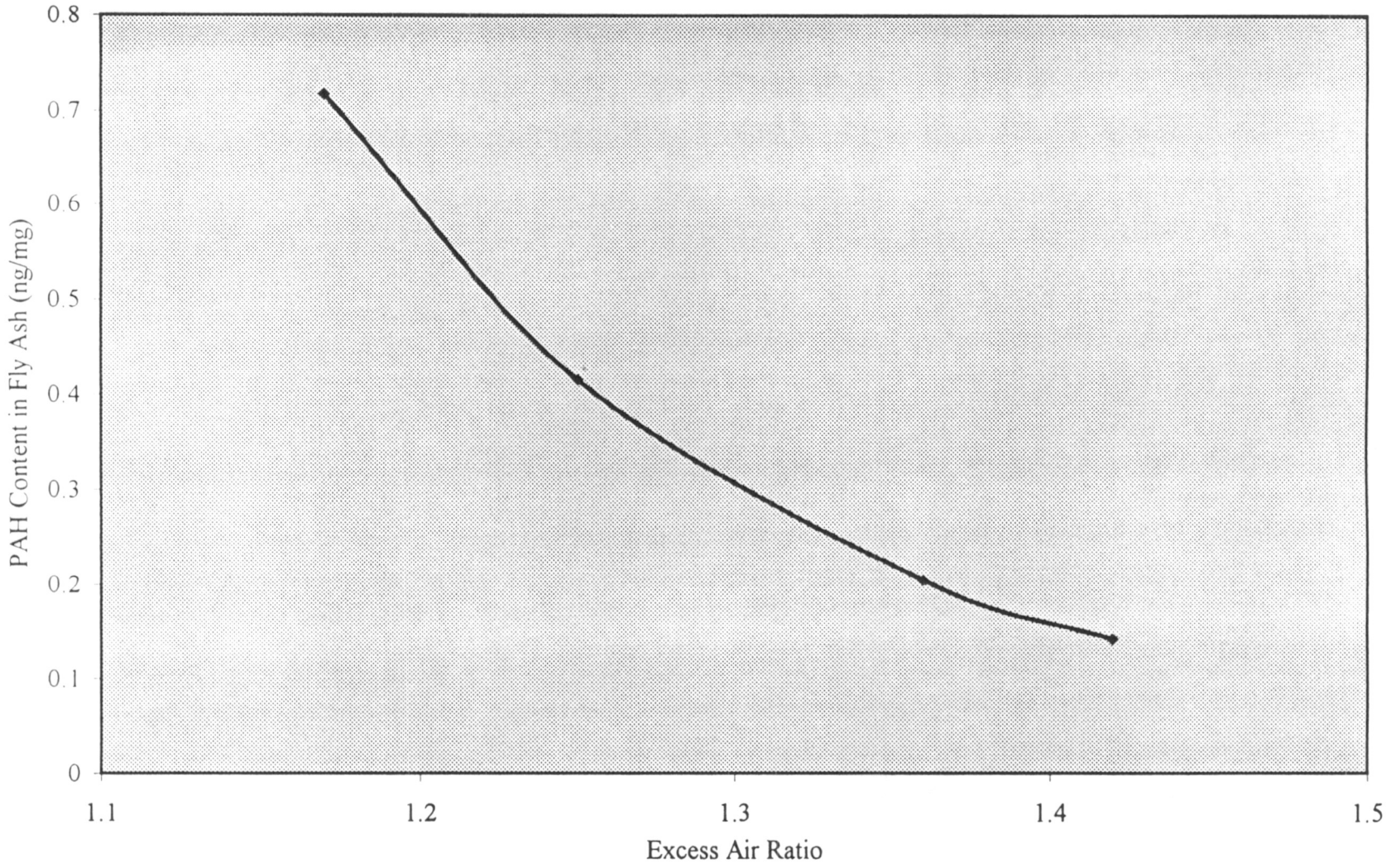

Figure 9. The effect of excess air ratio on the PAH content in the fly ash in an FBC system.

5. The Effect of the Air Flow Rate on the Content of PAHs in the Fly Ash for Coal 99626.

The combustion parameters for testing the effect of air flow rate on the content of PAHs in the fly ash for coal 99626 are listed in Table 16. Figure 10 illustrates clearly the relationship between the fluidizing velocity and the content of PAHs found in the fly ash. As the fluidizing velocity steadily increased, so did the content of PAHs in the fly ash. Thus, the elevated amount of air being forced into the combustor has a negative effect on the PAHs. This effect could result from the inadequate amount of residence time for the coal particles to completely burn out. Therefore, there is not enough time for decomposition of the large organic molecules in the coal. Basically, the lack of residence time in the combustor greatly reduced the combustion efficiency. As a consequence of the decrease in combustion efficiency, there were more PAHs detected.

Table 16. Combustion Parameters for Examining the Effect of Air Ratios on the PAH Content in the Fly Ash for Coal 99626.

	Coal 99626
Temperature (°C)	799
Coal Feeding Rate (rpm)	80
Secondary Air (m/s)	0.0
Bed Height (m)	0.865
Limestone Addition Rate (rpm)	14

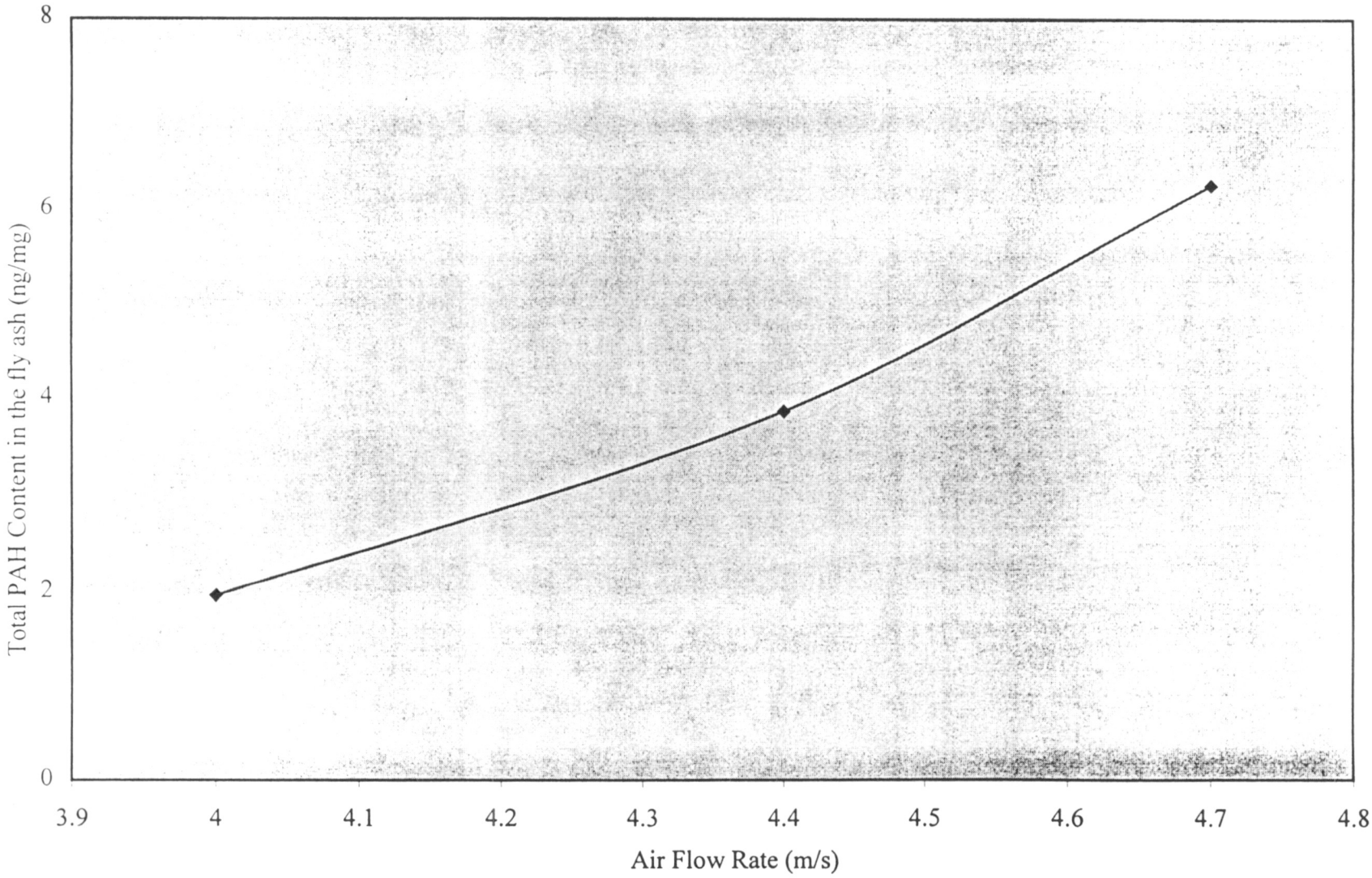

Figure 10. The effect of the fluidizing velocity on PAH content in the fly ash in an FBC system.

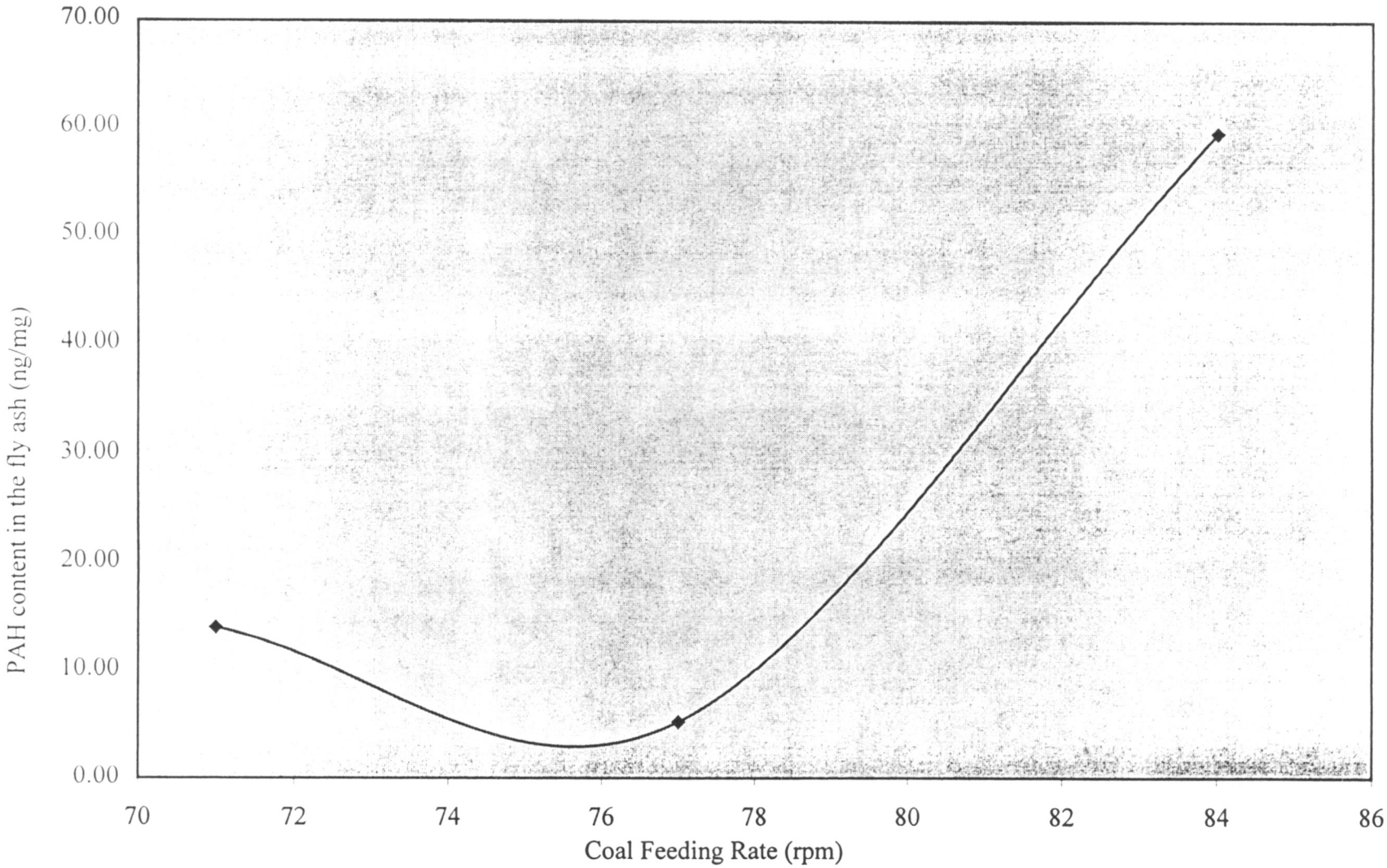

Figure 11. The effect of the coal feeding rate on PAH content in the fly ash in an FBC system.

The distribution of PAHs in the fly ash was examined to better understand the results of section B. This section primarily focuses on how the distribution of PAHs varies when examining the different parameters of the combustor. The PAHs were classified by the amount of rings they have in their structure. For example, naphthalene is a two-fused ring PAH. The EPA specified PAHs range in size from two rings to six rings (2R-6R). In addition to examining the distribution of the PAHs, this section also serves to correspond the data found in section B with the distribution. By relating these two phenomena, the mechanisms, which the PAHs were formed or released during coal combustion could be predicted. The combustion conditions and samples examined in this section were the same as the conditions and samples as in section B.

1. The Distribution of PAHs in the Fly Ash at Different Temperatures for Coal 97025 and Coal 99626.

When considering the effect temperature had on the number of rings in the PAHs in the fly ash, the most dramatic reduction was seen in the two and three fused-ring PAHs, as shown in Figures 12 and 13. This decrease could result from the smaller ringed species being more completely combusted at elevated temperatures. Yet, these smaller ringed species were still present in the fly ash at elevated temperatures. The mere presence of these rings in the fly ash could be attributed to the apparent but mild decrease in five and four fused-ring PAHs. These larger ringed species may have decomposed at the higher temperatures and produced the smaller ringed species detected.

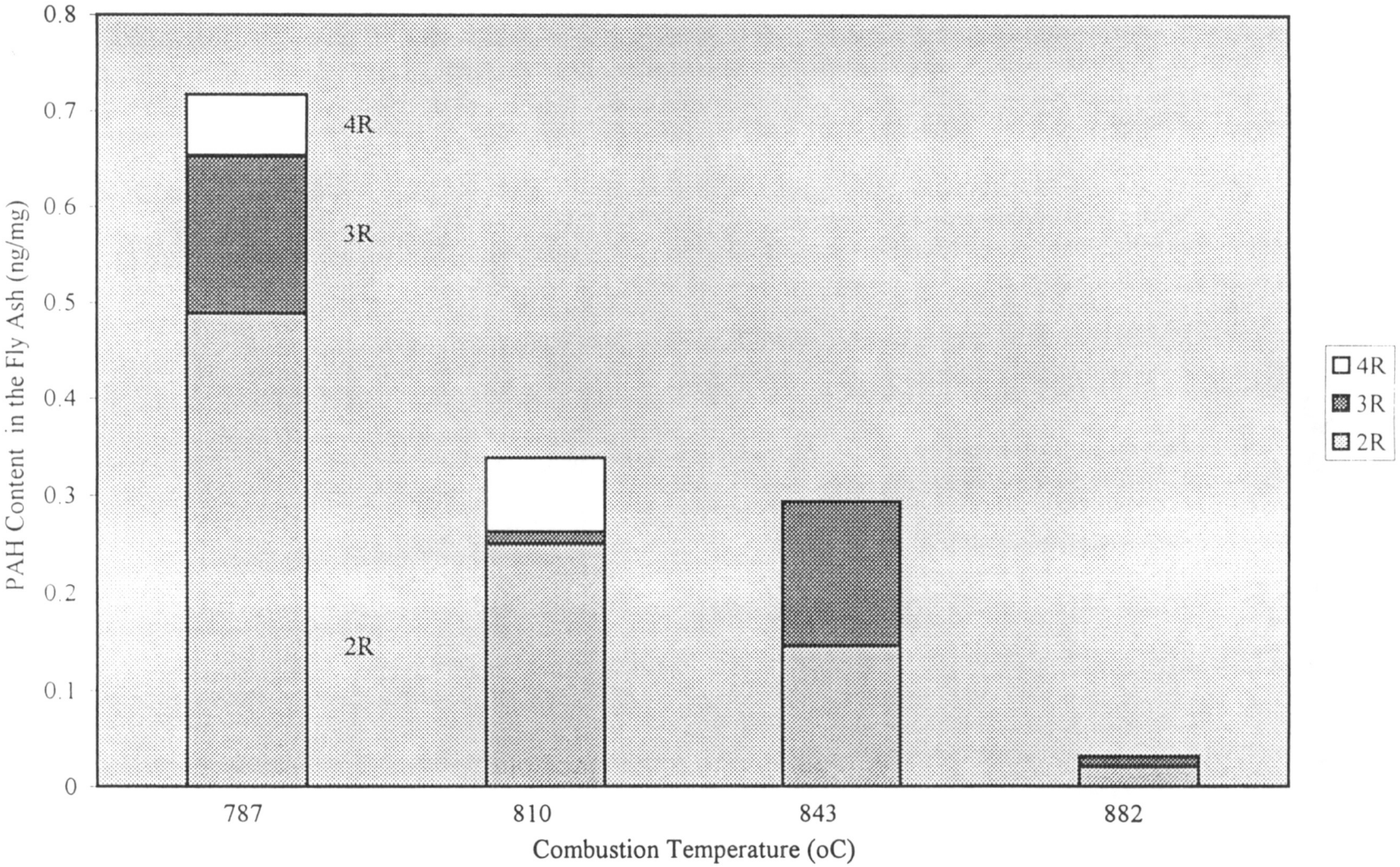

Figure 12. The distribution of PAHs in the fly ash at different temperatures in an FBC system.

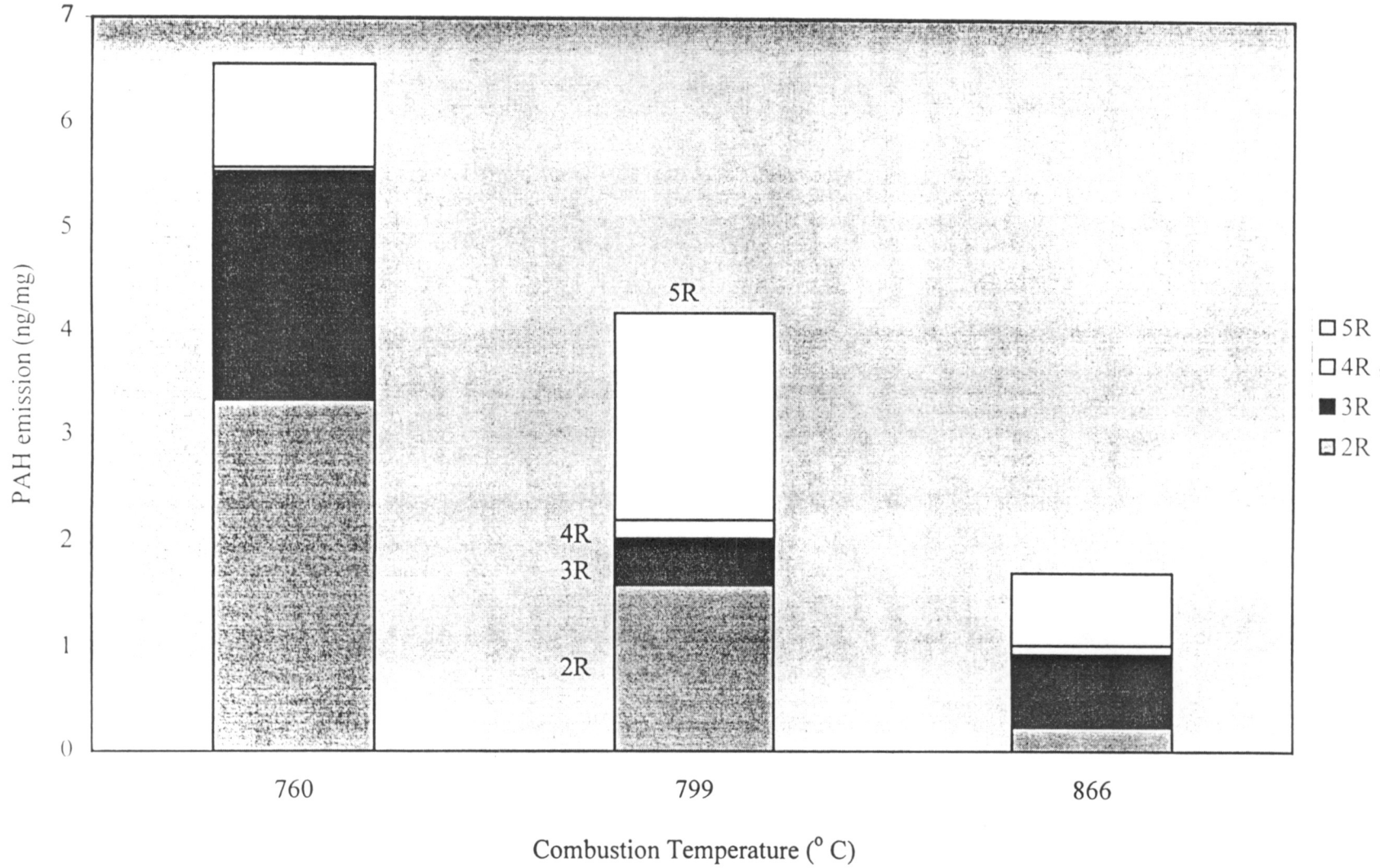

Figure 13. The distribution of PAHs in the fly ash at different temperatures in an FBC system.

The indication is that higher temperatures may provide the energy needed to break the macromolecular structure of the PAHs during coal pyrolysis and result in the smaller ringed PAHs. These speculations, which were based on the data investigated, of how the PAHs are varying in distribution and concentration are very plausible explanations of the sources of PAHs that were released during coal combustion. However, when it is well known that there are three major mechanisms that are forming or releasing PAHs in coal combustion, it is imperative that these also be studied as a source of PAHs. Based on the results in section B, at lower temperatures, the combustion was less efficient. It is known that the breakdown reaction is a mechanism that occurs during inefficient combustion conditions and results in the release of PAHs that were initially part of the coal matrix.[12] Observations made at 760°C in Figures 14 and 15 were characteristic of the breakdown reaction. At lower temperatures, there was an increased amount of two- and three-fused ring PAHs when compared to the concentration of the four or five fused-ring PAHs. The breakdown reaction could result in this massive release of the two- and three-fused ring PAHs that were initially part of the coal matrix.

Yet, as the temperature increased, so did the efficiency. And ultimately, at the highest temperature recorded there was a decrease in the overall concentration of each of the fused ring PAHs. But on the other hand, at 799°C, there was an increase observed in the five-fused ring PAHs. This increase could be attributed to the condensation reaction, a reaction in which, the two and three fused-ring PAHs condense to form the larger PAHs that were detected. Therefore, the formation of larger PAHs (5R) that was observed at 799°C could be an indication that the condensation reaction may have occurred at an

increased combustion efficiency; whereas, the breakdown reaction occurred during the more inefficient conditions in the combustor.

1. The Distribution of PAHs in the Fly Ash at Different Bed Heights for Coal 97025 and Coal 99626.

The distribution of PAHs in the fly ash at different bed heights is seen in Figures 14 and 15. The two figures clearly illustrate again that as the static bed height increased the overall concentration of PAHs found in the samples decreased, which was the same trend that was observed in section B. However, upon closer observation of the actual distribution of PAHs in both types of coals, it should be noted that at the lower bed heights the smaller (2R and 3R) PAHs were detected in higher concentrations than the larger (4R and 5R) PAHs. This trend was the same one that was represented in the temperature distribution figures. Therefore, the mechanisms that were responsible for forming or releasing the PAHs may be the same that were observed with the temperature. The meaning is that when efficiency of the combustor was low (0.65 m), the breakdown reaction could have occurred, which would release two and three fused-ring PAHs that were initially part of the complex coal matrix.

Yet again, as the bed height is increased, the operating conditions of the combustor are much more efficient, which yields a dramatic reduction in the two and three fused-ring PAHs. But in spite of this substantial decline, the four and five fused-ring PAHs were still detected at virtually the same concentrations until the highest efficiency was attained at 0.81 m. Again observing that as the efficiency was fluctuating between lowest and highest, the condensation reaction could have occurred, which would result in the formation of the four and five fused-ring PAHs that were detected. This

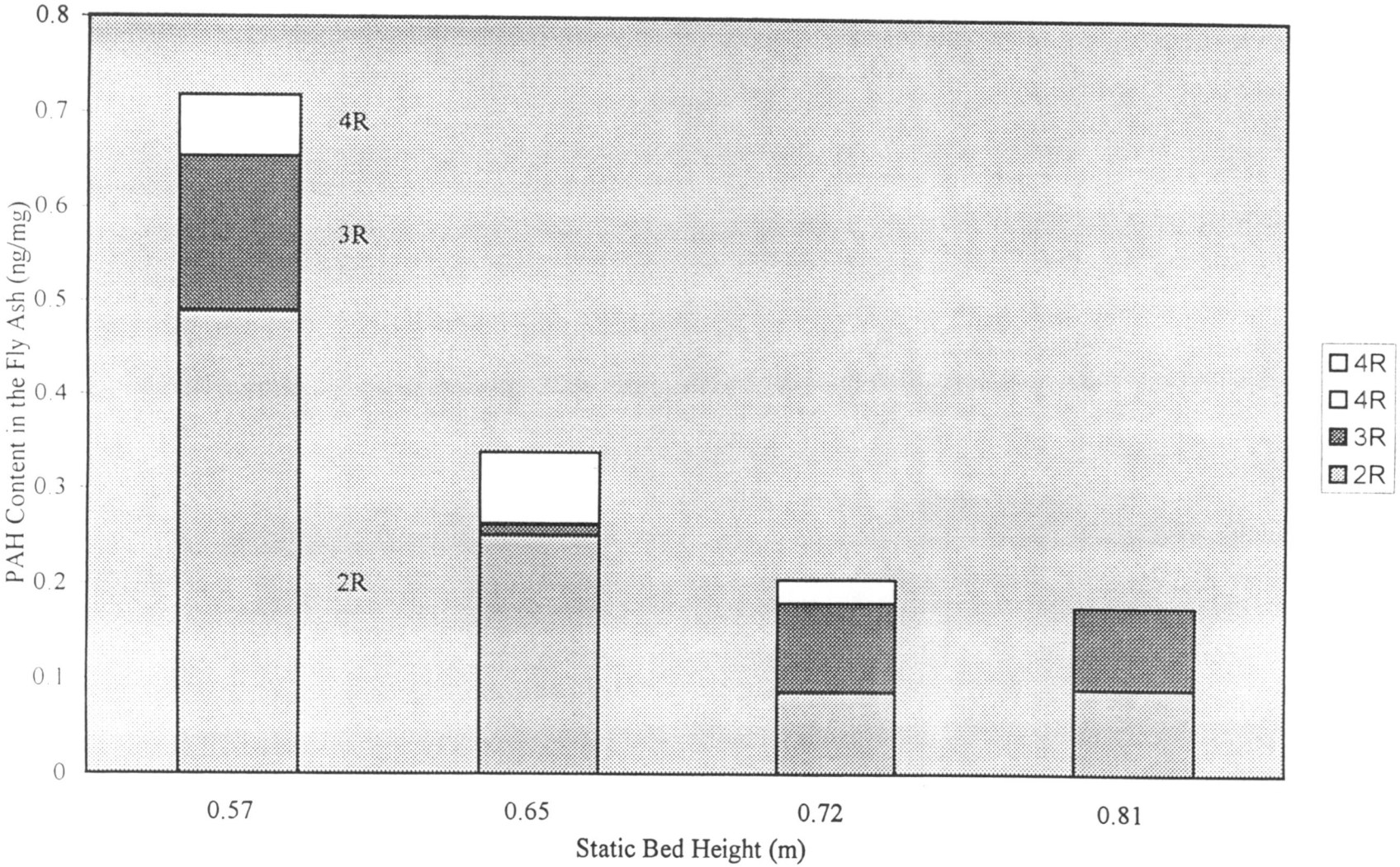

Figure 14. The distribution of PAHs in the fly ash at different bed heights in an FBC system.

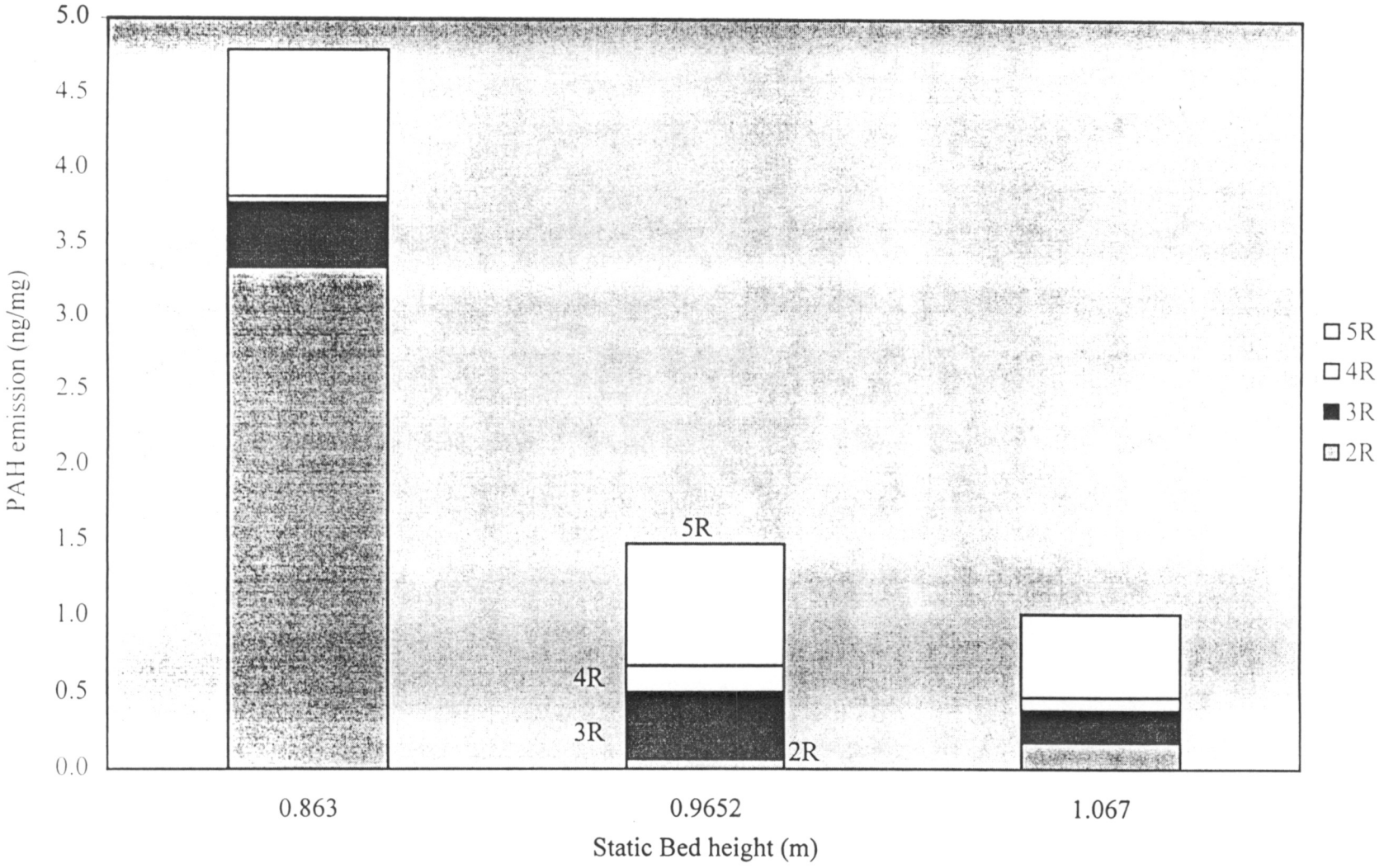

Figure 15. The distribution of PAHs in the fly ash at different bed heights in an FBC system.

behavior followed the same observation that was suggested previously. The breakdown reaction occurred during operating conditions in the combustor that were less efficient; whereas, the condensation reaction occurred in the more efficient operating conditions.

3. The Distribution of PAHs in the Fly Ash at Different Excess Air Ratios for Coal 97205.

The effect that the excess air ratio had on the number of rings in the fly ash can be seen in Figure 16. This figure illustrated that during the first plotted excess air ratio (1.17), two and three fused-ring PAHs were existing in large concentrations, while the larger PAHs were not as abundant in concentration. This observation was directly related to these previously made based on the distribution of PAHs that were examined for other parameters. Thus, this large concentration of smaller PAHs was indicative of the breakdown reaction occurring resulting in the release of the two and three fused-ring PAHs. However, as the excess air ratio increased and the combustion efficiency increased, the smaller PAH species were decreasing in concentration. The larger PAHs were also decreasing in concentration as the excess air ratio increases, yet at the 1.25 and 1.36 excess air ratio, the concentration of larger PAHs remained virtually the same. The indication is that the condensation reaction could have occurred to produce the larger PAHs species at the increased operating conditions.

4. The Distribution of PAHs in the Fly Ash at Different Fluidizing Velocities for Coal 99626.

Figure 17 shows the distribution of PAHs at different fluidizing velocities for coal 99626. As the fluidizing velocity increased, the total amount of two and three fused-

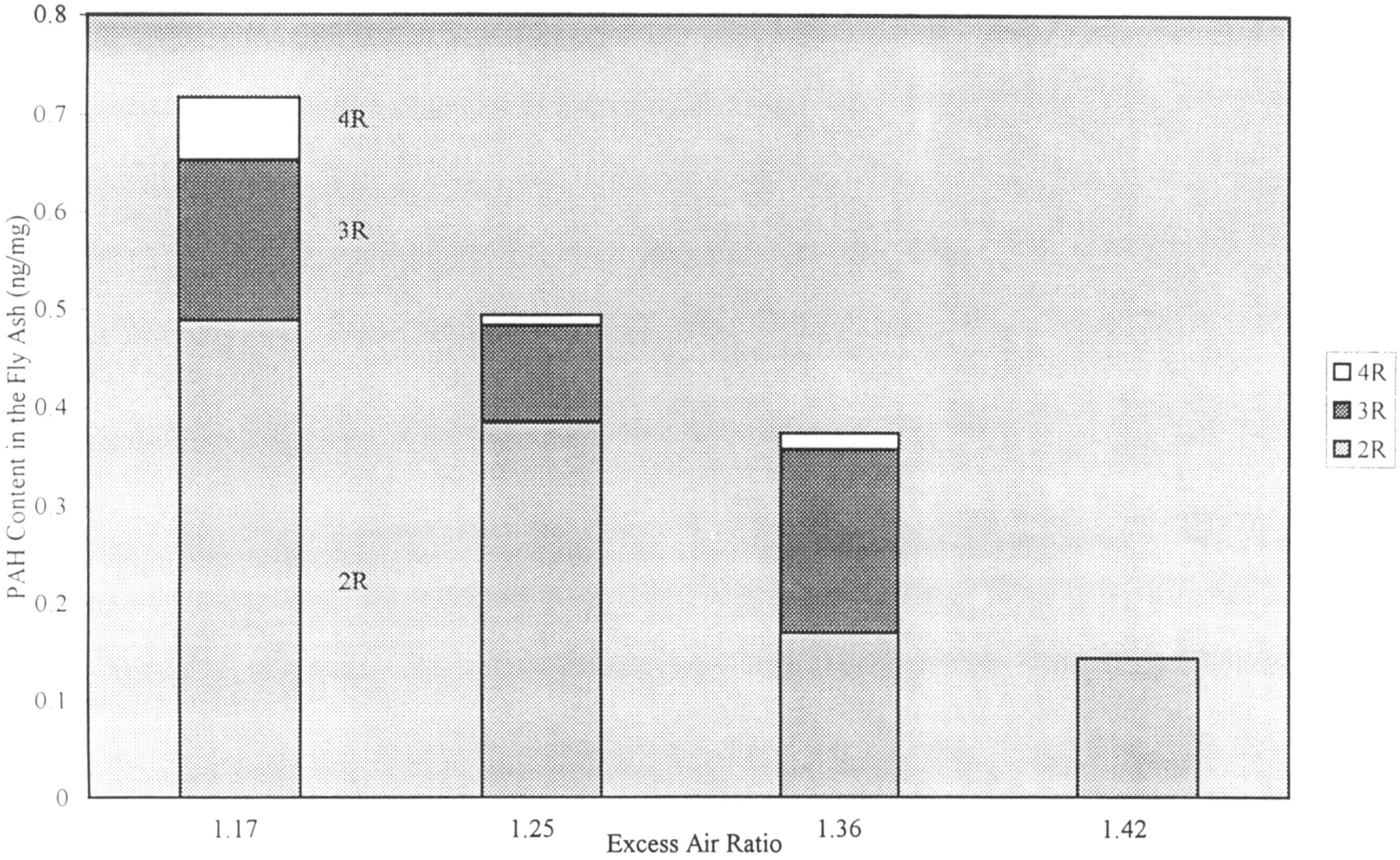

Figure 16. The distribution of PAHs in the fly ash at different excess air ratios in an FBC system.

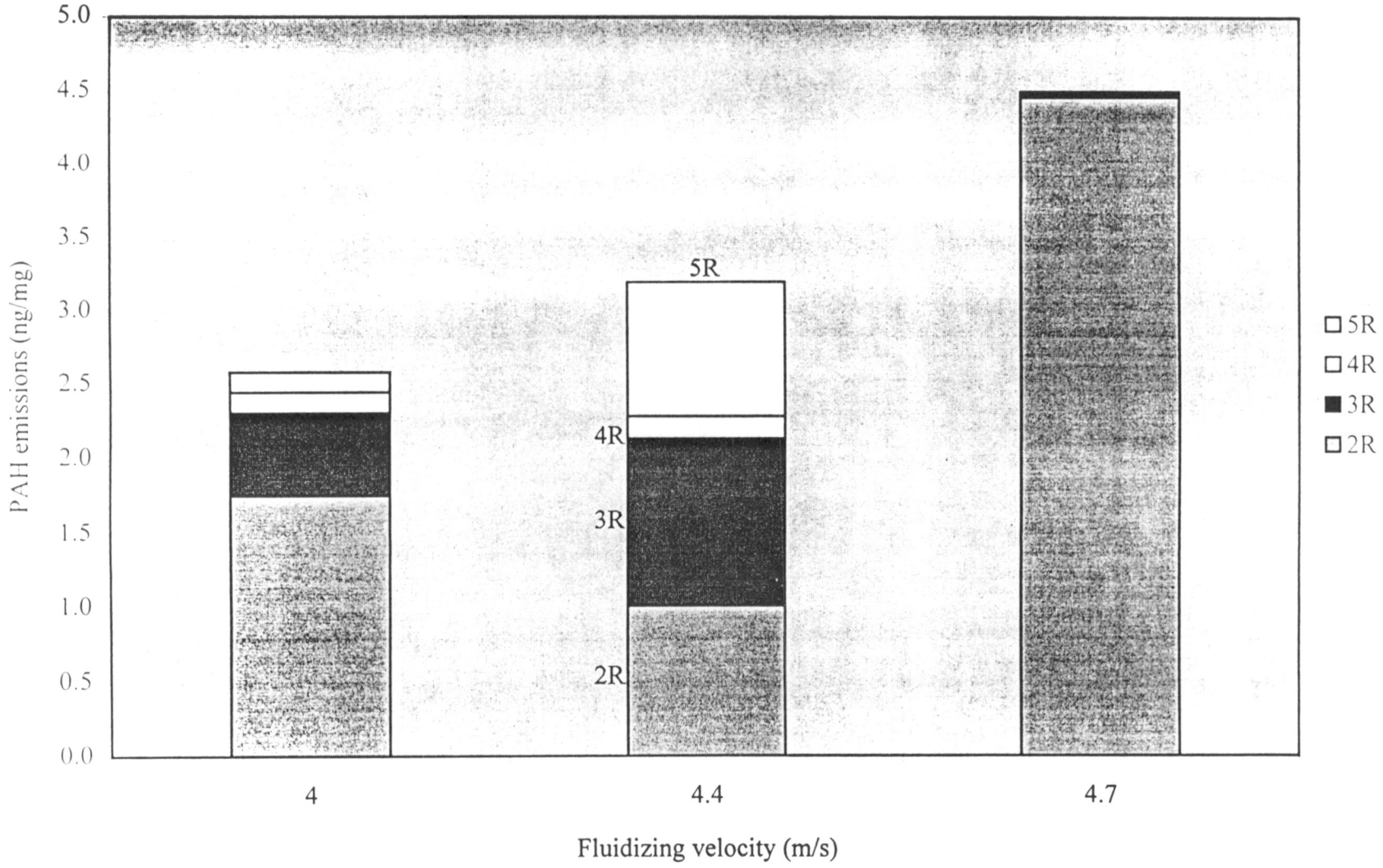

Figure 17. The distribution of PAHs in the fly ash at different fluidizing velocities in an FBC system.

ringed PAHs tremendously increased as well. However, the larger PAHs (4R and 5R) were completely gone at 4.7 m/s air ratio. This extreme increase in two fused-ring PAHs could be attributed to the decomposition of four and five fused-ring PAHs. Yet, it must also be considered that as the combustion efficiency decreased, there has been a trend of two and three fused-ring PAHs increasing. This trend has been observed in the previous parameters investigated and is indicative of the breakdown reaction occurring, which favors the release of the smaller PAHs. Also, it must be noted that at the more favorable conditions in the combustor, based on the fluidizing velocity, the larger PAHs were detected--once again, indicating that the condensation reaction mechanism could have occurred resulting in the larger PAHs.

5. The Distribution of PAHs in the Fly Ash at Different Coal Feeding Rates for Coal 99626.

The relationship between the coal feeding rate and the content of PAHs in the fly ash is shown in Figure 18. The two and three fused-ring PAHs in the fly ash were observed to dramatically increase as the amount of coal being fed into the bed of the combustor increased. As more coal was fed into the combustor, while maintaining constant temperature and bed height, the coal did not have a sufficient amount of time to react with the oxygen to form the desired products, CO_2 and H_2O. Therefore, at 84 lb/min, two and three fused-ring PAHs were rapidly generated due to incomplete burn out of the coal. However, there was not an increase in the four and five fused-ring PAHs at the accelerated coal feeding rate; in fact, they are not even detected. Thus, at increased coal feeding rates, the efficiency of the combustor was much lower than usual and the smaller PAH species were more likely to be released--indicative of the breakdown

reaction. The coal matrix released the smaller PAHs at the increased coal feeding rates, and then the PAHs do not have an opportunity to decompose or condense due to the lack of efficiency. Thus, resulting in the major increase observed in two and three fused-ring PAHs.

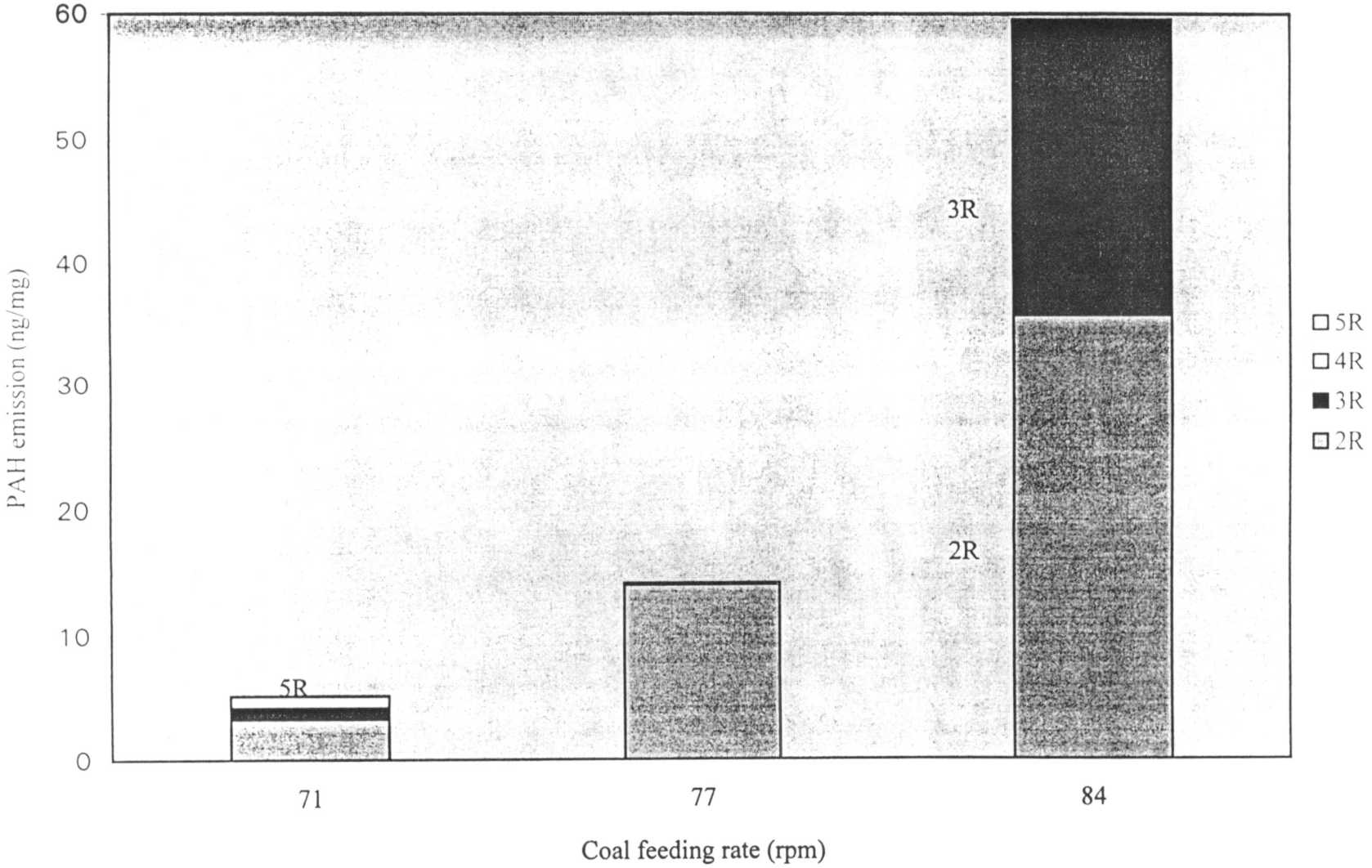

Figure 18. The distribution of PAHs in the fly ash at different coal feeding rates in an FBC system.

CHAPTER IV

CONCLUSIONS

Based on the data presented in this thesis, the following statements can be made.

1. The concentration of PAHs in the fly ash will decrease in a FBC system, when the combustor is operated at temperatures less than 850°C, increased static bed heights (>0.7 meters), lower fluidizing velocities, proper coal feeding rates, and increased excess air ratios.

2. The effects of combustion on reducing PAH content in the fly ash are as follows: excess air ratio >temperature > fluidizing velocity > static bed height Larger PAHs are more likely to be produced when combustion efficiency is low.

3. Smaller PAHs (2R and 3R) are produced as a result of the breakdown reaction during inefficient combustion conditions.

FUTURE STUDIES

Future studies that can be conducted based on the previous conclusions are as follows,

1. Development of an analysis method that can detect the mechanism that is responsible for releasing or forming the PAHs in the combustor.

2. Development of a model that can be used to replicate the release or production of PAHs in the combustor in order to prevent PAHs from being formed or released.

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